DISSERTATION

ANALYSIS OF INDUSTRIAL OILSEEDS: PRODUCTION, CONVERSION TO BIOFUELS, AND ENGINE PERFORMANCE FROM LARGE TO SMALL SCALE

Submitted by

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ABSTRACT

ANALYSIS OF INDUSTRIAL OILSEEDS: PRODUCTION, CONVERSION TO BIOFUELS, AND ENGINE PERFORMANCE FROM LARGE TO SMALL SCALE

Most of the biofuel produced in the U.S. as an alternative to petrodiesel is derived from soybean oil. Three major problems of using soy and other traditional biofuel feedstocks are: (1) the high commodity cost of the feedstock results in higher cost fuel than the petroleum equivalent, (2) land use requirements are too great to offset a significant portion of petroleum use, and (3) many traditional biofuel feedstocks also have food uses, which creates market competition and a "food versus fuel" debate. The problems above are addressed by exploring the feasibility of biofuel production from a new class of oilseeds known as industrial oilseeds, and industrial corn oil as a biofuel feedstock.

Industrial oilseeds are alternative low-cost oilseeds also known in the literature as low-impact oilseeds or non-food oilseeds. Due to their non-food nature, they steer us clear of any food versus fuel debates. They have several advantages over conventional oilseeds, such as a short growing season, high oil yield and quality, ability to thrive on marginal lands, and low water and fertilizer inputs. These advantages can equate to lower oil costs. Since these oils can be optimized for fuel instead of food, plant scientists can maximize the erucic and other long chain fatty acids, which increase fuel conversion rates and fuel quality. For several of these plant species, little or no engine research has been done; some in the agronomic community still consider some of these plants weeds. This research includes compression ignition engine performance and emissions studies, measurement of important fuel properties, and investigation into the feasibility of several fuel pathways.

Corn is not classified as an oilseed by the USDA; however, the corn kernel contains a small amount of oil (~3.5%) which can be extracted during the production of ethanol. Only the starch portion of a corn kernel is converted to ethanol; the remaining solids (including the oil) remain in the distillers grain coproduct. Recently, the ethanol industry has discovered economical methods to extract this corn oil from the meal stream. As corn oil extraction technology has matured and ethanol margins have tightened, the ethanol industry has started widely adapting this technology as an additional revenue-generating coproduct. Since most ethanol plants are non-food grade facilities, corn oil from an ethanol plant can also be categorized as an industrial oilseed. Corn oil represents a relatively new, abundant, and inexpensive source of biofuel feedstock. This research includes compression ignition engine performance and emissions of corn oil based fuels, feasibility of using corn oil as an on-farm biofuel feedstock, research into fuel production and processing methods, and measurement of important fuel properties.

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LIST OF ABBREVIATIONS

ARA = Applied Research Associates
BIC = Biofuels ISOCONVERSION
BSE = Brake Specific Emissions
BSFC = Brake Specific Fuel Consumption
CFPP = Cold Filter Plugging Point
CH = Catalytic Hydrothermolysis
CI = Compression Ignition
CLG = Chevron Lummus Global
CO = Carbon Dioxide
CRD = Crude
CSU = Colorado State University
DAQ = Data Acquisition
DI = Direct Injection
DOD = Department of Defense
DOE = Department of Energy
DOT = Department of Transportation
EC = Elemental Carbon
ECU = Engine Control Unit
EECL = Engines and Energy Conversion Laboratory
EGR = Exhaust Gas Recirculation
EISA = Energy Independence and Security Act
EMA = Engine Manufactures Association
EPA = Environmental Protection Agency
FA = Fatty Acid
FAME = Fatty Acid Methyl Ester
FID = Flame Ionization Detection
FTIR = Fourier Transform Infrared
GDP = Gross Domestic Product

GHG = Greenhouse Gas

GRAS = Generally Regarded As Safe

HC = Hydrocarbons

HDPE = High-Density Polyethylene

HEPA = High-Efficiency Particulate Absorption

HFRR = High Frequency Reciprocating Rig

HPCR = High-Pressure Common Rail

ICO = Industrial Corn Oil

ILUC = Indirect Land Use Change

IV = Iodine Value

KOH = Potassium Hydroxide

LCFS = Low Carbon Fuel Standard

LHV = Lower Heating Value

LOQ = Limit Of Quantification

MGY = Million Gallons per Year

NDIR = Non-Dispersive Infrared

NFPA = National Fire Protection Association

NMHC = Non-Methane Hydrocarbon

NMR = Nuclear Magnetic Resonance

NREL = National Renewable Energy Laboratory

NRSC = Non-Road Steady Cycle

OC = Organic Carbon

OSHA = Occupational Safety and Health Administration

PM = Particulate Matter

PPM = Parts Per Million

RBD = Refined, Bleached, Deodorized

RFS = Renewable Fuels Standard

SG = Specific Gravity

SMPS = Sequential Mobility Particle Sizer

SVO = Straight Vegetable Oil

TGB = Triglyceride Blend

ULSD = Ultra Low Sulfur Diesel

US = United States

USAF = United States Air Force

USDA = United States Department of Agriculture

USN = United States Navy

VGT = variable geometry turbocharger

VI = Virtual Instrument

VLC = Very Long-Chain

VOC = Volatile Organic Compound

WMO = World Meteorological Organization

Chapter 1. INTRODUCTION AND RESEARCH MOTIVATION

1.1 Use, Demand, and Cost of Energy

The world's increased use, demand, and cost of energy in terms of economic and environmental impact are all compelling motivations for this research. The United States (U.S.) consumes more than 18 million barrels of liquid fuel per day, primarily in the transportation sector [1]. Like the U.S. transportation sector, the U.S. Department of Defense (DOD) is a large consumer of liquid fuel. With use topping 12 million gallons per day, the DOD is the single largest consumer in the world, with the United States Air Force (USAF) accounting for more than 50% of the DOD's consumption [2].

Demand and competition for the world's energy has also increased in recent years. For example, in 2007 the world's energy consumption increased by 2.4%, with China's share of the growth at 52% [3]. India is another country with ever-increasing energy demands, with energy use increasing at the same pace with increases in gross domestic product (GDP). India's energy consumption nearly doubled from 2003-2013, and they are now the fourth largest user in the world [4]. Projections are for 56% growth in world energy consumption between 2010 and 2040. By 2035, China's projected energy consumption is 68% higher than the U.S.' [5]. These trends are shown in Figure 1-1.

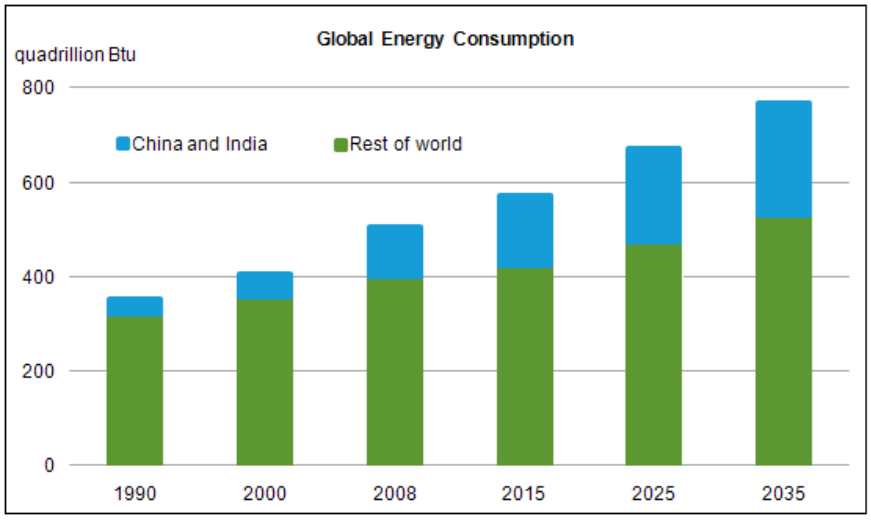

Figure 1-1. Projected global energy growth [5].

As competition for energy resources increases, another area of concern for the U.S. is the source of transportation fuels. The U.S.' proportion of imported oil increased from about 30% of consumption in 1970 to 56% in 2000, raising concerns about energy security and the vulnerability of the economy to disruption of oil supplies [6]. For the DOD, domestically sourced alternative fuels represent a reliable, secure and affordable supply of fuel for military missions. As stated by U.S. Navy (USN) Secretary Raymond Mabus: "Reliance on fossil fuels is simply too much of a vulnerability for a military organization to have" [7].

The large economic cost of liquid fuel is staggering. The U.S. transportation sector spends over $0.5 trillion annually on petroleum fuel [1]. For the DOD, the USAF alone spends nearly $9 billion per year on energy with more than 80% of expenditures for liquid fuel [8]. Due to the extreme quantities of fuel needed for military operations, price fluctuations heavily affect the DOD. Each time the price of oil goes up $10 per barrel, it costs the USAF an additional $600 million and the DOD $1.3 billion annually [9], [10].

The cost of petroleum fuel can also scrutinized from an environmental impact point of view, and is another reason to increase use of biofuels. In 2013, the World Meteorological

Organization (WMO) reported the highest atmospheric greenhouse gas (GHG) levels ever recorded, with levels increasing at an alarming rate. GHG levels in the atmosphere grew faster in 2012 than in the previous decade, and have increased to levels unprecedented in at least the last 800,000 years [11]. The WMO says the warming effect on our climate has increased by almost a third since 1990 [12]. As a result, global average temperatures might be 4.6 degrees higher by the end of the century than pre-industrial levels, leading to a more-extreme climate and rising sea levels [11]. Biofuels play an important role in reducing GHG emissions. Biofuels are created by converting biomass, biological material from living or recently living organisms, directly into liquid fuels. Biofuels are considered a carbon neutral fuel since plants intake the same amount of carbon dioxide (CO_2) during growth as released during combustion. Although exact level of reduction of life cycle emissions is under scientific debate, biofuels emit less GHG than the equivalent petroleum fuel [13].

In addition to GHG reductions, combustion of biofuels can have other net emission benefits (i.e. “tailpipe” emissions). For example, using the biofuel known as biodiesel (defined in section 1.7.4) typically reduces the amount of particulate matter (PM), carbon dioxide (CO), and hydrocarbons (HC) in the exhaust stream as compared to petrodiesel. In 2002, the EPA conducted a comprehensive analysis of the emission impacts of biodiesel using publicly available data, most of which was collected on heavy-duty highway engines, with curve fit values for the data collected shown in Figure 1-2.

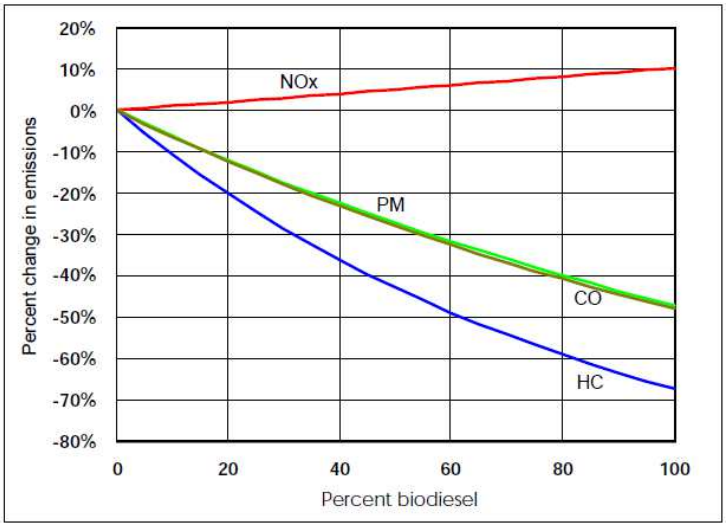

Figure 1-2. Average emission effects of biodiesel for heavy-duty highway engines [14].

To combat the issues outlined above, the U.S. Environmental Protection Agency (EPA) passed the Renewable Fuels Standard (RFS) program, created under the Energy Policy Act (EPAct) of 2005, and established the first renewable fuel volume mandate in the U.S. The program was expanded (RFSII) under the Energy Independence and Security Act (EISA) of 2007 to include diesel, in addition to gasoline. EISA increased the volume requirement of renewable fuel blending into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022. RFSII lays the foundation for achieving significant reductions of GHG emissions, for reducing imported petroleum, and encouraging the development and expansion of the U.S.' renewable fuels sector [15]. Several states have also mandated the use of biofuels. Minnesota first mandated biodiesel use in 2005, increased its blend requirements to B10 in 2014 (10% biodiesel and 90% petrodiesel), and will increase the requirement to B20 in 2018 [16]. In addition to usage requirements, many states have tax breaks and exemptions for biofuels. California recently passed a low carbon fuel standard (LCFS), which is a climate change driven standard, and may be the single largest emerging biodiesel market [17]. The LCFS considers the entire life cycle of fuel production and use and seeks to decrease overall CO_2 emissions.

The U.S. military has also initiated several measures to reduce its dependence on foreign sources of petroleum [18]. The USAF announced in 2008 that it plans to use alternative fuels for 50% of domestic aviation by 2016, approximately 400 million gallons per year [19]. The USAF's goal by 2030 is to be flying on alternative fuel blends that are cost competitive, domestically produced, and have a lifecycle GHG footprint equal to or less than petroleum [20]. The USN's goal for 2020 is to use alternative sources for half of all energy consumption afloat, which will require 300 million gallons of biofuels per year [21]. Due to the magnitude of consumption, any actions taken by the U.S. military to reduce energy consumption and procure alternative energy sources are significant in their potential impact for enhancing energy trends for the entire transportation sector [20].

1.2 Research Target Audience

This work will focus on biofuels made from oilseeds, grains that produce oil valuable for human use, with a concentration on industrial (non-food) oilseeds used to produce petrodiesel substitutes. The target audience for this research is both large-scale and small-scale users of biofuels. Large-scale includes the U.S. transportation sector and the U.S. military users as described above. The use of fuel in agriculture is significant, but smaller in scale as compared to the transportation and military end users. Although smaller in scale, farmers represent a very important role in the spread of the industrial oilseeds used in this research and the overall increased use of biofuels. Despite the motivation for increased use of biofuels from industrial oilseeds, the industry's commercial-scale crushing, fuel processing, and distribution infrastructure all need to mature. Some of the oilseeds discussed are so new that no commercial market exists [22]. If these new industrial oilseeds are ever going to be adopted, farmers will

need to take the lead in their production. Farm-scale fuel production could provide a local use for an oilseed until a commercial market matures.

1.3 Problem Statement and Research Objectives

As demand for domestically sourced fuels increased, the production of biofuel doubled from 2000 to 2005 and more than tripled from 2005 to 2010, and currently represents ~5% of U.S. consumption [23]. Despite these recent increases, most experts agree further expansion of biofuel use beyond mandated levels will be slow and most limited by feedstock costs, about 80% of the cost to make biodiesel [24], [25]. Soybeans represent 74% of the vegetable oil feedstock for biodiesel production. However, recent commodity costs in soybeans and other crops have been historically high, a major driving force behind the high cost of biofuels [26]. When the RFS came out in 2005, soybeans averaged $5.88 per bushel; in 2013, the average price of soybeans was $14.63 [27]. During this same period, corn prices went from $1.90 to $6.92 per bushel. Corn and soybeans also have food uses and face competition from those markets. Competition is not only from the food market; several hundred different products use soybeans. In 2012 alone, 45 new soy-based products were commercialized [28].

This research had several objectives. The first was to investigate the engine performance using biofuels produced from a category of oilseeds known as industrial oilseeds. Industrial oilseeds have several advantages over conventional oilseeds, which may reduce the cost of vegetable oil feedstock for biodiesel production. These industrial oilseeds only recently began use for commercial purposes and are still considered weeds by some in the agricultural community. Due to the newness of these vegetable oils, engine performance studies are limited or nonexistent. The second purpose was to investigate the effects of different biofuel types with respect to engine performance and fuel properties. An investigation into several fuel pathways

determined benefits and downsides to each. For reasons outlined above, the research was focused on farm-scale production and use of biofuels.

1.4 Industrial Oilseed Overview

Biofuel can be produced from various feedstocks, but the majority of petrodiesel substitutes are from plant oils. New sources of plant oil have emerged in recent years known as in the literature as “industrial oilseeds”, “low-impact oilseed crops”, or “non-food oilseeds” and include those oilseeds investigated in this research: carinata, camelina, and pennycress. This section outlines some of the benefits of industrial oilseeds.

With grains making up 80% of the world’s food supply, some view food and fuel as competing interests, and are concerned biofuels drive up the cost of food [29]. Jean Ziegler, an independent expert for the United Nations on food policy, called producing biofuels from food sources a “crime against humanity” and a “growing catastrophe against the poor” [13]. Industrial oilseeds are not suitable for human consumption (not generally regarded as safe (GRAS)) due to their high erucic acid content, so they eliminate any food versus fuel issues and eliminate market competition and fluctuations from the food market.

With respect to biofuel production, these industrial oilseeds offer many benefits over traditional oilseeds. For example, they have higher oil yield than soybeans, the most prominent traditional oilseed, resulting in more biofuel per acre. In addition to increased yield, oils designed for fuel requirements instead of food (high smoke point, taste, etc.) can have benefits of uniform long carbon fatty acid chains for increased fuel conversion rates and increased levels of monounsaturated fatty acid levels for better fuel quality [30].

Certain industrial oilseeds may allow increased production on marginal lands as compared to conventional crops. These oilseeds can grow with limited water, fertilizer, pesticides and other

inputs, with ongoing research by plant scientists in several areas of the U.S. to determine performance in these areas. These favorable properties allow industrial oilseeds to grow over a larger portion of available farmland in harsher conditions. A recent study estimated that only 6% of petrodiesel demand would be satisfied if all U.S. soybean production were dedicated to biodiesel [31]. Clearly, biofuel feedstock needs to expand and diversify if oilseed derived biofuels are to replace a larger portion of petroleum.

Due to the robustness of these new crops and short growing seasons, they are able to fit into several new cropping systems. These cropping systems better utilize the existing farmland in the U.S. and have the potential to produce millions of gallons per year of biofuel from the farmland already in production. A few examples of these cropping systems follow:

- Off-season cropping is growing a crop during a normally dormant production period. For the U.S., this generally means over the winter season (fall planted and spring harvested). In addition to the increased production, research indicates an off-season oilseed crop may reduce leaching of residual nutrients into ground water from row cropland [32].
- Oilseed cropping during a normally fallow period: Fallow cropland is land purposely kept out of production during a regular growing season, allowing one crop to grow using the moisture and nutrients of more than one crop cycle [33].
- Double-cropping is the practice of growing two or more crops in the same space during a single growing season. Relay cropping is a form of double cropping where different crops are planted at different times in the same field, and both crops spend at least part of their season growing together in the field [34].
- A cover crop is a crop planted primarily to manage soil fertility, soil quality, water, weeds, pests, diseases, biodiversity and wildlife in an agriculture ecosystem [35].

- A reduced water demand crop rotation can be used as part of a water leasing arrangement. A portion of a farmer's water allocation from irrigated farmland is leased for municipality uses, but the land can maintain productivity using dryland or limited irrigation methods [36].
- Oilseed cropping in the dryland portions of pivot irrigation: Much of the irrigation in the Western U.S. is by pivot irrigation; Nebraska alone has an estimated 43,000 pivot irrigation systems [37]. Without a corner system, pivot irrigation only covers $\pi/4$ (79%) of a square area. The remaining 21% of land would be a convenient area to grow oilseeds, since farm machinery is already in the area to farm the irrigated portion.

When used in one or more of the above cropping systems, these industrial oilseeds avoid any indirect land use change (ILUC) impacts currently being studied for other biofuels. ILUC studies focus on the unintended consequence of releasing more carbon emissions due to land-use changes around the world induced by the expansion of croplands in response to the increased global demand for biofuels [38].

Not competing with conventional cash crops not only helps keep the cost of production low, it might help increase the adaption of these oilseeds. Farmers are more apt to growing one of these oilseeds if it does not compete with their current cash crops, and the new crop involves low inputs (low risk).

These oilseeds allow for flexibility in planting date, which can benefit farmers. For example, many U.S. farmers have traditionally rotated soybeans and corn. Both crops are planted in the spring and mature at about the same time in the fall. This constraint limits the amount of land a farmer can manage due to labor and machinery demands. Adding a third crop, like an oilseed

that would be ready for harvest in the summer allows a farmer to spread their workload. Often this model has residual benefits by increasing yield 3-7% for the follow-on cash crop [34].

The industrial oilseeds discussed in this work are compatible with traditional farming equipment, important for widespread adoption. Several recent studies have investigated biofuel production from a wide array of other underutilized plant species. For example, common milkweed (*Asclepias syriaca*) is a perennial plant that grows on roadsides and undisturbed habitat, and generally considered a nuisance weed by farmers. Milkweed oil is suitable for biofuel production and the silk and sap have commercial applications [39]. However, milkweed seeds are currently harvested by hand from wild plants; large scale planting and harvest is not possible using existing farming equipment. The industrial oilseeds discussed in this work do not require a farmer to buy additional planting or harvesting equipment. The plants are also compatible with conventional oil extraction technology and oil filtering methods.

Unlike some other advanced biofuels in development, immediate implementation of these industrial oilseeds is possible without years of additional research and changes to the infrastructure of agriculture or transportation. The timeline for widespread adoption is much shorter than other more revolutionary forms of vegetable oils. For example, biofuel from microalgae lipids has a great deal of promise and received much attention in recent years. Algae are the most efficient biological producer of oil on the planet; some have estimated yield per acre potential as 200 times greater than conventional biofuel feedstock like soybeans [40]. Other positive attributes include the ability to grow in waste or salt water and recycle waste CO_2 from a power plant [40]. However, most experts agree fuel from algae at a large scale is a decade away and currently large scale production of these fuels is not feasible due to high cost [41]. The DOD recognizes the potential for algae based fuel, but its price has limited testing and market

expansion. For example, the USN came under congressional scrutiny for paying $425/gallon for 20,000 gallons of algae-based fuel in 2010 [42].

1.5 Industrial Oilseeds Used In Research

This section will provide a brief introduction and background for the industrial oilseeds used as feedstock for biofuel production in this research.

1.5.1 Camelina

Camelina (*Camelina sativa*) is a broadleaf oilseed flowering plant belonging to the Brassicaceae (mustard) family. It is in the same family as the more well-known oilseeds rape and canola and food crops like broccoli, cabbage, and cauliflower. Camelina was cultivated in Europe for oil and animal feed periodically for at least 3,000 years but declined in popularity by the 1940's due to the introduction of the oilseed rape [43], [44]. Camelina, with its high content of unsaturated fatty acids (~ 90%), was more difficult and expensive to hydrogenate than rape oil and this led to its decline [43]. Camelina grows optimally in temperate climates and is well adapted to the more northerly regions of North America, Europe, and Asia. It can be grown in a variety of climatic and soil conditions as a spring or summer annual or as a biennual winter crop. Camelina has several beneficial agronomic attributes: a short growing season (85–100 days), tolerance of cold weather, drought, semi-arid conditions, and low-fertility or saline soils. Growing camelina uses less water, pesticide, and fertilizer than other traditional commodity oilseed crops [45].

Camelina seeds typically contain 38-45% oil and produce a high quality meal with approximately 45% protein when crushed; revenue generation from the meal is an important factor in determining oilseed profitability [46]. Camelina has renewed attention in the U.S. and Europe, which is in part due to its positive agronomic attributes but also due to its high levels of

linolenic acid, one of the essential OMEGA-3 fatty acids generally found in substantial quantities only in linseed and fish oils [47].

Camelina oil was first evaluated as a straight vegetable oil (SVO) fuel in a modified indirect injection naturally aspirated diesel engine in 2003 [48]. Camelina oil was later evaluated as a potential biodiesel feedstock in 2005, with successful conversion, measurement of key fuel properties, and a one oil-change interval vehicle trial [49]. The USAF and USN began experimenting with camelina biojet fuel in 2010 [50]. A comprehensive characterization of camelina biodiesel was performed based on the U.S. and European standards in 2013 [51]. Figure 1-3 shows camelina images.

Figure 1-3. Camelina [52].

1.5.2 Carinata

Carinata (*Brassica carinata*) is alternative energy crop belonging to the Brassicaceae (mustard) family. Carinata is originally from Ethiopia where it has been grown as an oilseed for many years. It is closely related to rapeseed (*Brassica napus*), the most common oilseed in Europe, and researchers have been developing it in recent years as an alternative to rapeseed and other traditional oilseeds. Many Canadian farmers are now planting it on their traditionally marginal canola farm ground [53]. Due to its background in Ethiopia, the plant is able to grow in

harsh growing conditions and is extremely well suited to production in semi-arid areas. It has shown good resistance to stressors such as insects, disease, heat, and drought [54]. Agronomic studies have confirmed that carinata adapted better and was more productive both in adverse conditions (clay- and sandy-type soils and semi-arid temperature climate), and under low input cropping systems when compared with rapeseed [55]. Researchers have also been improving the harvestability characteristics of carinata, such as lodging and pod shatter resistance, which makes it compatible with straight cutting [54].

Carinata seeds typically contain 45% oil with 35% protein content in the residual meal, and can produce 200 gallons of biofuel per acre [30], [53]. Carinata produces a 22-carbon erucic acid, as opposed to a typical 18-carbon oleic acid molecule found in canola and other oilseed crops, giving it more carbon in the fatty acids for fuel production [56].

In 2003, carinata was converted to biodiesel and performance tested using a direct injection passenger car diesel engine [55]. In 2012, the USAF teamed with other research partners to evaluate carinata biojet fuel; the evaluation culminated in the world's first jet aircraft flight powered by 100% renewable fuel [53], [57], [58]. Carinata is shown in Figure 1-4.

Figure 1-4. Carinata [59].

1.5.3 Pennycress

Field Pennycress (*Thlaspi arvense* L.) is a winter annual found throughout the Americas belonging to the Brassicaceae (mustard) family. Pennycress is a common agricultural weed, listed as "noxious" in several U.S. states, and can cause serious yield losses in field crops and can contaminate hay and grain feed [60], [61]. Although still widely considered a weed, it has recently received attention for its potential as an alternative energy crop. Pennycress seeds typically contain 32-36% oil with 33-35% protein content in the residual deoiled meal [62]. Pennycress' high seed yield, seed oil content, and suitability for off-season production make pennycress an ideal source of oil for biofuel [62]. The early harvest date of pennycress compared to other winter annual oilseed crops makes it suitable for harvesting two crops (pennycress and soybeans) in one year in most of the upper Midwestern U.S. [62]. Those farmers using pennycress as an off-season crop for the first time in 2012 saw an additional $100/acre in revenue, with future projections at $175/acre [63].

Pennycress was studied as a potential replacement for rapeseed oil for certain industrial applications as early as 1944 [64], but was not evaluated as a potential biodiesel feedstock until 2009 [65]. Pennycress seeds were crushed for the first time at a pilot scale in 2009 using seeds harvested from a wild stand in Illinois [62]. Pennycress is shown in Figure 1-5.

Figure 1-5. Pennycress [66].

1.6 Conventional Oilseeds Used In Research

The focus of this research was on industrial oilseeds. However, conventional oilseeds continue to have a prominent place in the market. Along with industrial oilseeds, several of these conventional plants are now being used in nontraditional cropping systems. Like the industrial oils, these conventional oils were also converted to biofuel through new fuel pathways for this research.

1.6.1 Corn

Corn is the most widely grown crop in the U.S., with over 400,000 U.S. farms harvesting 84 million acres annually [67]. Field corn (*Zea mays* L.) is a type of maize whose leafy stalk produces ears that contain the grain, called kernels. The dent corn variety (*indentata*) has many uses; it is an important source of livestock feed and had several food uses such as corn flour, corn oil, and high fructose corn syrup. The USDA does not classify field corn as an oilseed; however, the germ of its kernel contains a small amount of oil (~3.5%). During the production of ethanol, corn oil can be extracted and used for the production of biofuels. Most ethanol plants are nonfood-grade facilities so the extracted oil cannot be used for human consumption, and makes corn oil an industrial oil when processed at these facilities. Corn is shown in Figure 1-6.

Figure 1-6. Corn [68].

1.6.2 Soybeans

The soybean (*Glycine max*) is a species of legume (Fabaceae family) widely grown worldwide for its edible bean, which has numerous uses. Its seeds are an important source of oil and protein for both human and animal consumption. Soybeans are the second most produced crop in the U.S., with nearly 74 million harvested acres annually. Soybeans represent 90% of U.S. oilseed production and 50% of oil production worldwide [67]. Soybeans dominate both the U.S. biodiesel and food-oil market, representing 74% of vegetable oil feedstock and 65% of oil consumed [67]. Soybean seeds contain ~40% protein and 20% oil and typically produce 65 gallons of biofuel per acre (1 bushel ≈ 1.5 gallons of biofuel) [69], [70]. When soybean seeds are processed for oil, a valuable high protein meal remains and livestock consume nearly 30 million tons annually [71]. The soybean plant is shown in Figure 1-7

Figure 1-7. Soybean [72].

1.6.3 Canola

Canola is a cultivar of rapeseed (*Brassica napus*). It was bred from rapeseed in the 1970s by researchers in Canada. These researchers were able to develop canola to have low levels of glucosinolates and erucic acid, enabling canola oil to become a widespread food oil. Canola seeds are high in oil content (40-44%) and produce a high quality livestock meal when crushed. Canola oil is also used to produce biodiesel, and is the third most used feedstock behind soy and corn oil in the U.S. Canola can be planted in the fall or spring, giving it great flexibility as a rotation crop. Several researchers have studied canola as a potential closed loop oilseed. For example, a city could pay local farmers to grow canola, extract the oil and incentivize its use by local restaurants, recollect used cooking oil from the restaurants, and finally convert the oil to biodiesel for use in the city bus system [73].

Researchers in the U.S. have been investigating the feasibility of relay cropping canola and soybeans. The cold tolerant canola is planted in the early spring and begins growing immediately. Later soybeans are planted to the same field. The canola's shorter growing season allows it to be harvested in the summer. With the majority of canola seeds being high on the plant, the combine header can harvest the canola seeds but cuts above the soybeans. The young

soybeans continue to grow through the canola stubble and are ready for harvest in the fall. The combined biofuel yields of canola (~110 gallons per acre) and soybeans (~45 gallons per acre) greatly improve productivity on existing land [74]. In addition to the additional crop, this model may reduce erosion, and disrupt pest and weed cycles [34]. Canola is shown in Figure 1-8.

Figure 1-8. Canola [75].

1.6.4 Sunflower

Sunflower (*Helianthus annuus*) is an annual plant native to the Americas. It possesses a large flowering head. The heads consist of many individual flowers, which mature into seeds. Sunflower seeds and sunflower oil are widespread cooking ingredients. Sunflower (oilseed type) seeds contain 38-50% oil and approximately 20% percent protein [76]. Leaves of the sunflower plant can be used as cattle feed along with the residual meal from oil production. The stems have industrial uses, such as paper production.

Sunflowers can efficiently use water, which may become very important in Colorado and other areas of the Western U.S. as water resources become more limited. Researchers with the USDA found that under limited and timed irrigation, sunflower has a unique ability to produce a higher yield than under unlimited irrigation as shown in Figure 1-9.

Figure 1-9. USDA Sunflower Trial: (L to R) unlimited irrigation, irrigation in R1-R5 growth stage, and irrigation in R4-R5 growth stage [77].

1.7 Fuel Pathways Used in Research

Several vegetable oil to fuel conversion options, or fuel pathways, exist to create biofuels from vegetable oil. This section highlights the conversion options evaluated as petrodiesel substitutes in this research.

1.7.1 Direct use of Straight Vegetable Oil (SVO)

Using straight vegetable oil (SVO) as a diesel fuel substitute is not a fuel conversion – it is a lack of conversion. SVO has been used directly as a fuel in diesel engines since their inception, with the first documented use in 1900 [78], [79]. SVO performance has been well studied for many vegetable oils. The bulk of scientific literature has shown long term use of SVO can have negative effects in modern engines, most of which are tied to its high viscosity [80]. These effects can be partially mitigated by decreasing service intervals and through engine modifications. Typically fuel pumps are upgraded and fuel heaters are placed in auxiliary fuel tanks to reduce the viscosity of the oil [81].

1.7.2 Dilution of SVO

The blending of SVO with petrodiesel is often referred to "dilution of SVO" or "SVO as a diesel fuel extender". SVO and petrodiesel blends mixtures have also been well studied in the literature, with mixed recommendations on their use. For example, as a result of a 600-hour test using a John Deere 6-cylinder, 6.6 L, direct injection, turbocharged engine, it was found that a 1:2 volumetric blend of soybean SVO to petrodiesel would be suitable as a fuel for agricultural equipment [82]. In contrast, a 200-hour test using a Ford 3-cylinder, 2.59 L, direct injection engine found a 1:3 volumetric blend of soybean SVO to petrodiesel would not be suitable as a fuel due to excessive carbon deposits [83].

Like the direct use of SVO, the use of dilution of SVO has been found not satisfactory in several studies for both direct and indirect injection diesel engines over long intervals [84], [85], [86]. High fuel viscosity, poor cold flow characteristics, polymerization during combustion, carbon deposits in the combustion chamber, and lubricating oil thickening are problems observed during testing [80], [87]. For these reasons, the Engine Manufactures Association (EMA), U.S. Department of Energy (DOE), and U.S. EPA have released statements discouraging the use of SVO in neat form or mixed with petrodiesel regardless of blend level [88], [89], [90], [91]. Despite this, widespread use of SVO and dilution mixtures continues worldwide, with ongoing research for niche applications, such as the off-road use of fuel in agriculture, fuel for other remote users such as third world countries where users are isolated from fuel supplies but fuel is needed to run grain mills and local vehicles, or for use in times of fuel shortages [92].

1.7.3 Triglyceride Blend (TGB)

To reduce the problems outlined in sections 1.7.1 and 1.7.2, SVO can also be blended with other less viscous fluids (other than petrodiesel). The literature shows SVO has been blended

with ethanol, methanol, n-butanol, 2-octanol, 2-propanol, other solvents, or combinations of these fluids [86], [93]. For some combinations, a surfactant is needed to ensure emulsion stability if a mixture contains two or more liquids that are normally immiscible [94]. Various naming conventions have been used for these blended fuels.

A triglyceride blend (TGB) is the naming convention used at Colorado State University (CSU) for a biofuel formed when SVO is blended with another less viscous solvent and the resulting solution is used as a biofuel. This research uses motor gasoline with various ethanol contents (E0-E85) and renewable naphtha as blend agents. The U.S. DOE defines motor gasoline as a complex mixture of relatively volatile hydrocarbons blended to form a fuel suitable for use in spark-ignition engines with a boiling range of 122 to 158 °F [95]. Naphtha is defined as light distillates with an approximate boiling point range between 122 and 400 °F blended further or mixed with other materials to make high-grade motor gasoline, jet fuel, solvents, petrochemical feedstocks, and other uses [96]. The origin of SVO and gasoline mixtures is unclear and has not been extensively studied or documented in scientific literature, although TGBs have been in use by some U.S. farmers for several years [97]. Naphtha as a SVO blending agent is also previously undocumented in scientific literature.

1.7.4 Biodiesel (B100)

Triglycerides, often abbreviated as TG, are the main constituents of vegetable oil [98]. A triglyceride (i.e. triacylglycerol) is a molecule with a glycerol backbone to which are attached three fatty acid groups (esters), typically 14-22 carbons in length with varying degrees of unsaturation [99]. Biodiesel is produced by a reaction of the esters in vegetable oil (or animal fat) with an alcohol in the presence of a catalyst to yield mono-alkyl esters and glycerol, which is removed [100]. The resulting fuel, “biodiesel”, is comprised of mono-alkyl esters of long chain

fatty acids and is registered with the U.S. EPA as a fuel and a fuel additive under Section 211(b) of the Clean Air Act (40 CFR Part 79) [100]. Biodiesel has been extensively studied in the literature, with most finding engine performance generally favorable with emissions benefits in most categories except NO_x [101]. Most OEMs now approve biodiesel and petrodiesel blends at varying levels (e.g. B5) in their vehicles and farm equipment [102]. Blending is recommended due to the difference in biodiesels' energy content, cold flow properties, storability, materials compatibility, and other factors as compared to petroleum [102].

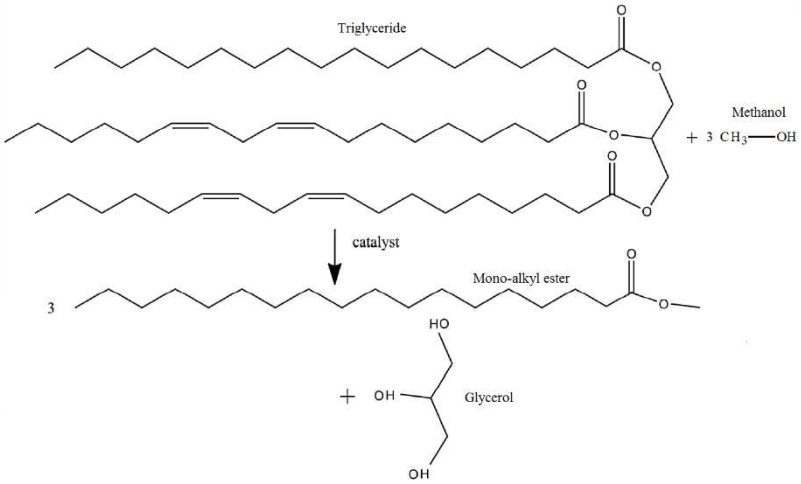

Figure 1-10. Converting triglyceride (TG) in vegetable oil to fatty acid methyl esters (FAME) via transesterification.

1.7.5 Renewable Diesel (R100)

Vegetable oil can also be converted into non-ester renewable fuels that are pure hydrocarbons and indistinguishable from their petroleum counterparts. These fuels, referred to as renewable diesel, meet the standards of ASTM D975 (Standard Specification for Diesel Fuel Oils) and are therefore considered "drop-in" alternatives to petroleum. Renewable diesel eliminates the need for blending, equipment modifications, or infrastructure changes. It has the same naming convention as biodiesel in that R20 is 20% renewable and 80% petrodiesel. There are three primary methods for creating renewable diesel: hydrotreating, hydrothermal processing,

and indirect liquefaction [103]. This section will briefly discuss hydrotreating since it was used to produce the R100 fuels in this study.

Hydrotreating (hydrodeoxygenation) is the process of reacting a feedstock with hydrogen in the presence of a catalyst under elevated temperature and pressure in order to change the chemical properties of the feedstock and remove the oxygen [104]. Recently, several companies have begun to use hydrotreating to convert vegetable oils into distillate fuels (there are several variations and naming conventions for the process). Hydrotreating produces distillate fuel with properties very similar to petroleum. The main byproduct is propane, which has increased value compared to glycerol [104].

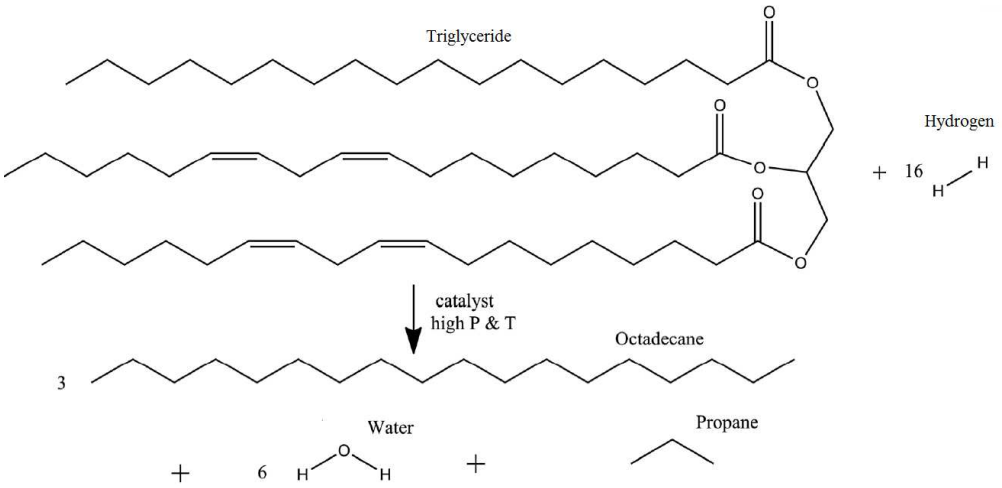

Figure 1-11. Hydrodeoxygenation of triglyceride to non-ester renewable fuels [105].

1.8 Conclusions

The industrial and conventional oilseeds that were used in this research, and the motivation for their adoption, were introduced in this chapter. The industrial oilseeds may have advantages over conventional options, both in production and in fuel conversion. Cropping systems were also discussed to outline how these oilseeds can increase production on existing lands. Finally, the fuel pathways used in this research were also introduced.

Chapter 2. COMPRESSION IGNITION ENGINE PERFORMANCE AND EMISSION EVALUATION OF INDUSTRIAL OILSEED BIOFUEL FEEDSTOCKS CAMELINA, CARINATA, AND PENNYCRESS ACROSS THREE FUEL PATHWAYS[1]

2.1 Introduction

2.1.1 Need for biofuels and economical feedstocks

As the world's use, demand, and cost of energy in terms of economic and environmental impact steadily increase, the need for renewable fuels is greater than ever. The U.S. transportation sector's mandated use of biofuels attempts to alleviate these energy impacts [106]. The U.S. military has also turned to biofuels as an important alternative to petroleum fuel. The purchase of fuel from foreign markets for military operations has been identified by senior military leadership as a key vulnerability [20]. All military branches have recently set use goals of alternative fuels that are cost competitive, domestically produced, and have a lifecycle greenhouse gas footprint equal to or less than petroleum. Additionally, Department of Defense (DOD) officials have said that any alternative fuels for DOD operational use must be derived from a non-food crop feedstock [18].

Like the larger scale U.S. transportation sector and military users, fuel is very important to the agriculture community. Farm use of distillate fuel oil is significant, especially in the agricultural centers of the U.S. and other parts of the world. For example, farm use represents more than 20% of total fuel consumption in Iowa [107]. The prices paid by farmers for fuel and other energy-based inputs nearly tripled from 2002 to 2005, and continue to steadily increase [108], [109]. The United States Department of Agriculture (USDA) found higher energy-related production costs generally lower agricultural output, raise prices of agricultural products, and

[1] Manuscript published in *Fuel* 136 (2014) 143–155 by A.C. Drenth et al. [137]

reduce farm income [110]. In response to these increased fuel input costs, several farmers have decided to grow and produce their own biofuels on the farm. This gives them greater control over one of their largest input costs. Farm-scale fuel production allows a farmer to avoid retail margins and transportation costs of both the crop and fuel. It also has several collateral benefits, such as the ability to control the quality of their fuel and gives them protection from fuel shortages at critical times like planting and harvest [92], [111], [112], [113].

Despite the need for these biofuels, a few issues hinder future growth. One major issue is the high cost of traditional biofuel feedstock. Feedstock cost represents 75–80% of the cost to make biodiesel [24], [25], [114]. As shown in Figure 2-1, recent grain commodity costs in soybeans and other conventional feedstocks have been historically high and are driving this limitation. Another issue is that land use requirements of conventional feedstocks are too great to offset a significant portion of petroleum use. A recent study estimated that only 6% of petrodiesel demand would be satisfied if all U.S. soybean production were dedicated to biodiesel [31]. Finally, many traditional biofuel feedstocks also have food uses, creating a ‘‘food versus fuel’’ debate. With grains making up 80% of the world’s food supply, some view food and fuel as competing interests, and are concerned biofuels drive up the cost of food [13], [29].

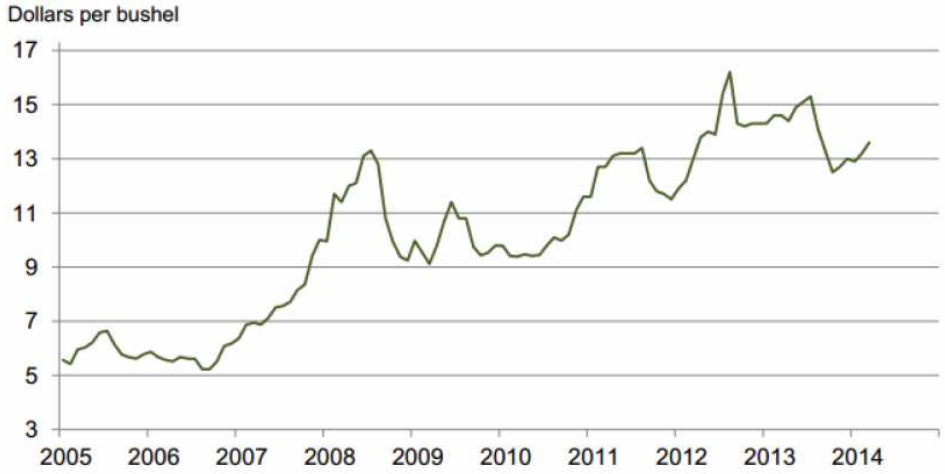

Figure 2-1. U.S. prices received for soybeans [27].

2.1.2 Industrial oilseeds

Industrial oilseeds are alternative low-cost oilseeds that have great potential to increase biofuel use by alleviating the problems outlined above. Due to their non-food nature, they avoid any food versus fuel debates. In addition to their high oil yield and quality, industrial oilseeds have several agronomic advantages over conventional oilseeds such as a short growing season, cold weather tolerance, ability to thrive on marginal lands (salinity, fertility), and low input requirements (water, pesticide, fertilizer). These advantages can equate to lower oil production costs [13], [43], [44], [45], [48], [49], [55], [62], [65], [115], [116].

The industrial oilseeds of primary focus for this research were camelina (*Camelina sativa* L.), carinata (*Brassica carinata*), and pennycress (*Thlaspi arvense* L.). These oilseeds were selected for their ability to grow well in much of the U.S., their compatibility with existing agriculture and fuel infrastructure, and potential to see widespread adoption in the near term. Several traditional oils used for biofuels were also included in the research: soybean, canola, sunflower, and corn. These traditional options were included, not only as a performance baseline, but also because this research included previously unexplored fuel pathways.

The agronomic attributes of the industrial oilseeds camelina, carinata, and pennycress make them compatible with off-season cropping, fallow cropping, relay cropping, or other non-traditional cropping systems. These cropping methods allow for the production of industrial oilseeds without competition with other major cash crops, and can increase biofuel feedstock production on existing farmlands at low input costs. Not competing with conventional cash crops not only helps to keep the cost of production low, it may help the popularity of these oilseeds spread.

A few examples of how oilseeds are integrated into these cropping systems are given below. However, some plant scientists are exploring other interesting alternatives for oilseeds in different cropping systems. Camelina is being grown by farmers in the Western U.S. and Canada during a period of the year that is normally the fallow portion of a winter wheat rotation. It has an estimated renewable fuel yield potential of an additional 100 million gallons per year (MGY) without increasing the total number of cultivated acres [117]. Carinata is being explored as an off-season crop to soybeans, peanuts, and cotton in the Southern U.S. Yield estimates from this cropping system in Florida alone is 40–100 MGY [32]. Pennycress is being explored in the Midwestern U.S. as an off-season crop separating a corn-soybean rotation. Yield potential for this rotation is 4 BGY, which would be a significant increase over current U.S. total biodiesel production [118].

The U.S. military has expressed interest in these industrial oilseed feedstocks, and began flight trials with camelina based jet fuel in 2010 and carinata based jet fuel in 2012 [58]. The United State Air Force (USAF) Chief Scientist recently identified the use of efficient and abundant non-food source biofuels as a game changing technology in energy generation for 2011–2026 [119]. For this new class of oilseeds, the industry's crushing, fuel processing, and distribution infrastructure all need to mature. Senior DOD leaders have called this the classic ''chicken and the egg'' scenario. Defense Production Act Title III Programs have been established focusing on the creation of an economically viable production capacity for advanced drop-in biofuels [22]. Even with these programs, currently most U.S. farmers that would want to grow camelina, carinata, or pennycress would not be able to market the crop locally. Using the crop to produce on-farm fuel and livestock feed gives a grower a local market for these crops until a commercial market matures.

2.1.3 Fuel pathways for vegetable oil

Vegetable oil can be converted to a biofuel for use in compression ignition (CI) engines through several fuel pathways. Using straight vegetable oil (SVO) directly as a diesel fuel substitute is one of the oldest biofuels [78]. SVO as a petrodiesel substitute has been well studied. Several studies have found SVO engine durability issues during long-term use. Carbon deposits in the combustion chamber and lubricating oil thickening are problems observed during testing [80]. SVO and petrodiesel mixtures have also been researched for several feedstocks and volumetric ratios. While recommendations on using SVO as a petrodiesel fuel extender have been mixed, several studies have also shown unfavorable results [82], [84], [120], [121], [122], [123], [124], [125], [126]. Due to the documented reduction in engine durability during long-term use in unmodified engines, SVO and SVO + petrodiesel blends were not used in this engine performance study.

One of the main concerns with using SVO directly as a fuel in CI engines is that several fuel properties, especially viscosity, vary considerably from petrodiesel. One way researchers have addressed this is by blending SVO with various thinning agents other than petrodiesel such as ethanol, methanol, 1-butanol, other solvents, or a combination thereof. In some cases, the blending agent is normally immiscible with SVO and a surfactant is required. There are other names and variations in the literature for this type of blend including hybrid fuels, cosolvents, emulsions, and others [93], [94], [127], [128]. In addition to the reduction in viscosity, research indicates other potential combustion, fuel property, and emission benefits for some blend types [80], [127], [129].

A triglyceride-blend (TGB), is a variation of this blending/dilution method, formed when SVO is mixed with another less viscous fuel (other than petrodiesel), and the resulting solution

used as a petrodiesel substitute. E10 gasoline was used to form the TGBs in this study. TGB is a naming convention/abbreviation used at Colorado State University (CSU) for this type of biofuel, and was used throughout this report. Peer reviewed literature found on this type of blend is extremely limited, although several U.S. farmers have been successfully using SVO-gasoline blends for several years [97]. Using gasoline as a blending agent has several benefits: it is readily available, has high energy content, inexpensive, and is completely miscible and stable with SVO. Like other blends of this nature, as compared to biodiesel, producing TGBs are fast, have low energy inputs, do not create waste products, and do not require a catalyst [94]. TGBs change the physical properties of SVO to be more similar to petrodiesel so they can be used directly in unmodified engines. This research investigates the feasibility of TGBs as a suitable on-farm fuel, and compares engine performance to petrodiesel and other biofuels.

Biodiesel was also used as fuel pathway during this evaluation. Conversion of triglycerides to esters (biodiesel) also changes fuel properties to be more similar to petrodiesel. Biodiesel from conventional feedstocks has been well studied, but engine performance testing using industrial oilseeds camelina, carinata, and pennycress as a biodiesel feedstock is limited. Most research has focused on biodiesel conversion and quantification studies [53], [65], [118], with some CI engine performance data studies using camelina SVO [118].

Recently, another alternative method use to convert triglycerides to fuel known as renewable diesel holds great promise as a renewable drop-in alternative to petroleum. The U.S. military has already identified this fuel pathway as most compatible with military operations [18]. CI engine testing using these industrial oilseeds as a renewable diesel feedstock is also limited.

The main objectives of this research project were to conduct compression ignition engine performance testing and emissions evaluation using industrial oilseeds (camelina, carinata, and

pennycress) and conventional oilseeds feedstocks (soybean, canola, sunflower, and corn) comparing multiple fuel pathways. The research explored if using industrial oilseeds have any engine performance differences as compared to conventional biofuel feedstocks. The research also investigated how underexplored fuel pathways like TGB and renewable diesel compared to petroleum and biodiesel.

2.2 Experimental setup

2.2.1 Test fuel preparation

All testing was performed at the Engines and Energy Conversion Laboratory (EECL) at CSU. The vegetable oils used in this evaluation were obtained from various sources; most oils were mechanically extracted via screw or expeller oilseed presses and lightly filtered. The sources of oil and other testing materials are shown in Table 2-1. Oil extraction and fuel preparation methodology was kept consistent with typical farm-scale fuel procedures. Since most farm-scale producers do not have access to large scale refining, crude oil was used as the biofuel feedstock unless otherwise noted. To evaluate oil feedstock refinement's effect on engine performance and emissions, biofuels produced from both crude and refined, bleached, and deodorized (RBD) soybean and corn oil were used in testing. Since vegetable oil quality and properties can vary with season, location, and other factors, the same batch of oil was used to produce each type of biofuel.

The TGBs used in the evaluation were formed by filtering SVO with a 10 μm polypropylene filter, then blending the SVO with E10 at a 3:1 volumetric ratio. The resulting TGB was vigorously agitated in a high-density polyethylene (HDPE) container before filtering again to 1 μm.

SVO was converted to biodiesel in via transesterification (alcoholysis) in a research-scale reactor in the EECL. Crude vegetable oil was added to the reactor, recirculated, and heated to 60 °C. In a separate container, methoxide was prepared from methanol and potassium hydroxide (KOH) at a 1:5 M ratio and 1 wt. % KOH. After adding the methoxide to the oil, the mixture was recirculated for two hours to help the conversion to fatty acid methyl esters. Following the reaction and settling, the lower glycerol layer was separated. The biodiesel was then water washed until a neutral pH was obtained, air dried, and filtered to 1 μm before engine testing.

Applied Research Associates (ARA) and Chevron Corporation created the renewable diesels in this evaluation. ARA provided two variations of their Renewable, Aromatic, Drop-in Diesel (ReadiDiesel™) produced through their Catalytic Hydrothermolysis (CH) process. One ARA described as ‘‘heavy’’ and is intended to meet the Navy Distillate Diesel Fuel specification (NATO symbol F-76). The other was described as their ‘‘full boiling range’’ fuel, and is intended as a drop-in, #2 petrodiesel substitute. Both were created using carinata oil as feedstock. Chevron labeled their renewable diesel as ‘‘experimental hydrotreated renewable diesel’’, and was created from camelina oil. Hydrotreating of vegetable oils and the Catalytic Hydrothermolysis (CH) process is described in other publications [130].

Table 2-1. Source of testing materials.

Material	Source	Location
Carinata Oil	Agrisoma Bioscience, Inc.	Saskatoon, SK, Canada
Camelina Oil	ClearSkies, Inc.	Bozeman, MT, USA
Pennycress Oil	Arvens Technology, Inc.	Peoria, IL, USA
Soybean Oil	South Dakota Soybean Processors, LLC	Volga, SD, USA
Corn Oil	Glacial Lakes Energy	Watertown, SD, USA
Canola Oil	Painted Rock Farms	Stratton, CO, USA
Sunlower Oil	Prarie View Farms	Penokee, KS, USA
Carinata R100	Applied Research Associates, Inc.	Panama City, FL, USA
Camelina R100	Chevron Corporation	Richmond, CA, USA
Methanol, 99.85 wt. % purity	Industrial Chemicals Corporation	Arvada, CO, USA
Potasium Hydroxide, ACS Grade	Avantor Performance Materials, Inc.	Center Valley, PA, USA
Diesel Fuel, Grade No. 2-D S15	Team Petroleum, LLC	Fort Collins, CO, USA
E10 Gasoline, ethanol % certified	Agfinity Cooperative	Eaton, CO, USA
Polypropylene Filter Bags	Duda Energy LLC	Decatur, AL, USA

2.2.2 Test engine setup

Engine performance and emission assessments were conducted using a 4-cylinder, 16 valve, turbocharged and intercooled, 4.5 l, 175 hp, John Deere 4045 PowerTech Plus test engine. The test engine, shown in Figure 2-2, is configured with a variable geometry turbocharger (VGT), exhaust gas recirculation (EGR), and electronically controlled high-pressure common rail (HPCR) fuel injection and meets Tier 3/Stage IIIA emissions specifications. The test engine is connected to an eddy current dynamometer (Midwest Inductor Dynamometer 1014A). The dynamometer and dynamometer controller (Dynesystems Dyn-LocIV) were used to load the engine and maintain a constant engine speed and load for each test fuel. The engine's standard fuel tank was filled with dyed off-road petrodiesel used for engine warm-up and cool-down, and was use to flush the engine between test fuel runs. A three way solenoid valve and lift pump is used to deliver test fuels from an auxiliary fuel tank. Fuel flow is measured by a coriolis meter (Micro Motion 2700R11BBCEZZZ) and verified gravimetrically by a precision balance (Mettler-Toledo MS32000L). A Kistler Instrument Corporation PiezoStar® pressure sensor (6056A41) with glow plug adaptor (6542Q128) was installed in the glow plug port of cylinder 1

to record in-cylinder pressure data. A custom system designed in the EECL uses a National Instruments PXI-1002 connected to Kistler Type 5010 charge amplifiers to record high-speed combustion data from the in-cylinder pressure. An incremental encoder is connected to the crankshaft on the engine to provide crankshaft position as well as instantaneous engine RPM. Pressure and temperature values for several engine locations can be independently controlled and values logged via National Instrument's data acquisition hardware (DAQ) and LabVIEW virtual instrument (VI) software. Engine control unit (ECU) data was also recorded.

Figure 2-2. 4.5 L 175 HP John Deere 4045 at the EECL.

2.2.3 Exhaust gas sampling and emissions measurement

The test engine exhaust stream is sampled by two different probes. One averaging probe extracts exhaust for gaseous emissions measurement. Criteria pollutant measurements were made using a Rosemount 5-gas emissions analysis system that includes chemiluminescence measurement of nitric oxide (NO), nitrogen dioxide (NO_2) and total oxides of nitrogen (NO_x) (Siemens NOx-MAT 600), flame ionization detection (FID) of total hydrocarbons (THC) (Siemens FIDAMAT 6 Total Hydrocarbon Analyzer), paramagnetic detection of oxygen (O2) (Rosemount NGA 2000 PMD), and non-dispersive infrared (NDIR) detection of carbon monoxide (CO) and carbon dioxide (CO_2) (Siemens ULTRAMAT 6). In addition to the 5-gas

emissions analysis system, a Fourier Transform Infrared (FTIR) spectrometer (Thermo Fisher Scientific Nicolet 6700) was used to obtain speciated measurement of hydrocarbons through C4, and a variety of hazardous air pollutants and volatile organic compounds (VOCs) such as formaldehyde, acetaldehyde, and acrolein.

2.2.4 Particulate matter sampling and measurement

The second exhaust probe samples a small portion of the exhaust stream for particulate measurements. All of the PM measurements were taken after the exhaust sample is diluted with clean air in a mini dilution tunnel. The dilution air was first cleaned by a high-efficiency particulate absorption (HEPA) filter and then filtered by an activated charcoal filter. A turbine flow meter was used to measure the flow rate of clean dilution air. A valve located downstream of the turbine flow meter was used to control the dilution ratio. The mixture is passed through a residence chamber to simulate particulate mixing with ambient air. Then a portion of the flow is pulled from the base of the residence chamber through a PM10 cyclone, which eliminates particulates larger than 10 μm.

The remaining particulates (PM10) are collected on 46.2 mm Teflon filters (Whatman PLC 7592-104) filter downstream cyclone. The Teflon filters are weighed before and after the test using a microbalance (Mettler-Toledo MX5) with a precision of 1 μg. A second cyclone, also at the base of the residence chamber, is used to collect PM onto 46.2 mm quartz filters (Whatman PLC 1851-047). The quartz filters were subsequently analyzed using a Sunset Labs OC/EC Analyzer to determine elemental carbon (EC) and organic carbon (OC) ratios. Finally, a Grimm Technologies Sequential Mobility Particle Sizer (SMPS) was also connected to the dilution tunnel. The SMPS was used to measure particle size distributions from 10 to 1000 nm. The basic

engine test schematic is shown in Figure 2-3 and the mini dilution tunnel schematic is shown in Figure 2-4.

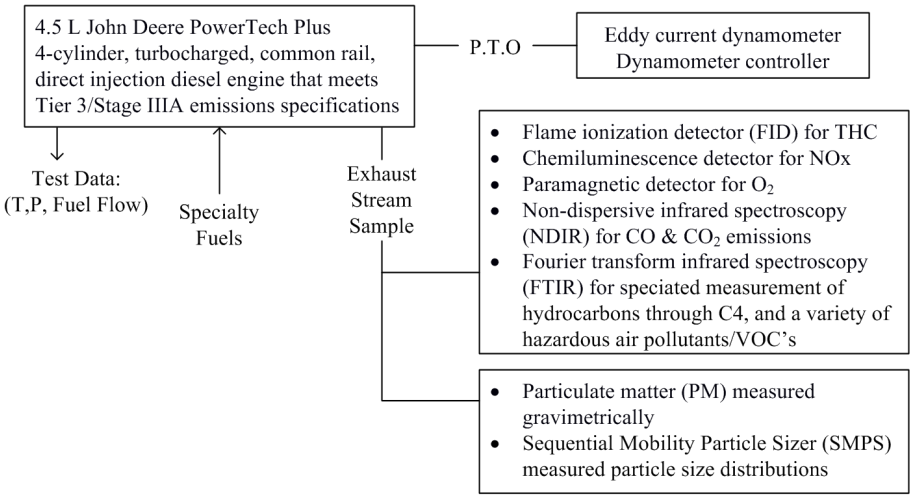

Figure 2-3. Basic schematic of engine performance test setup.

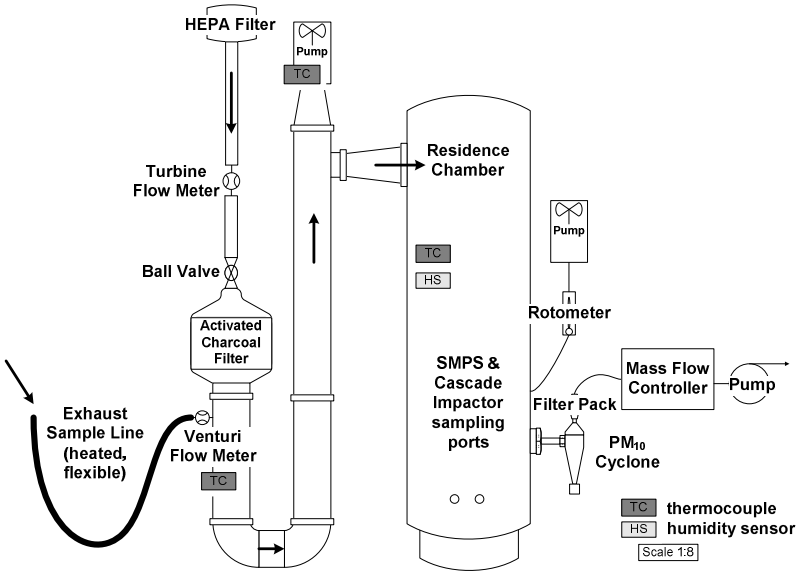

Figure 2-4. Schematic of mini dilution tunnel at EECL [131].

2.2.5 Testing procedure, operating conditions, and fuel properties

Engine performance and emissions data was recorded at 50% load and intermediate speed setpoints (250 N-m and 1700 rpm), which corresponds to mode 7 of ISO 8178 Non-Road Steady Cycle (NRSC) [132]. After switching to test fuel, fuel flow was adjusted to hold desired load, and the engine was allowed to stabilize. Once steady state was achieved, data was collected for

5-min intervals. Between each run, the engine was operated on petrodiesel to purge the system of test fuel. Petrodiesel data was recorded at the beginning, middle, and end of the evaluation. Seven feedstocks were evaluated, using three fuel pathways, and for two refinement levels as shown in Table 2-2. Not every combination was available due to feedstock availability. Engine operating conditions during the testing period are shown in Table 2-3. Several physical properties of the test fuels were measured in the Advanced Biofuel Combustion and Characterization Laboratory (ABC^2) in the EECL. These fuel properties, and the instrument used to measure them, are shown in Table 2-4.

Table 2-2. Engine performance test runs.

RUN #	FUEL TYPE	FEEDSTOCK TYPE	REFINEMENT LEVEL
1	DIESEL	Petroleum	
2	B100	Carinata	Crude
3	TGB		
4	$R100_1$		
5	$R100_2$		
6	B100	Camelina	Crude
7	TGB		
8	R100		
9	B100	Pennycress	Crude
10	TGB		
11	DIESEL	Petroleum	
12	B100	Soybean	Crude
13	B100		RBD
14	TGB		Crude
15	TGB		RBD
16	B100	Corn	RBD
17	TGB		RBD
18	TGB		Crude
19	B100	Canola	Crude
20	TGB		
21	B100	Sunflower	Crude
22	TGB		
23	DIESEL	Petroleum	

Notes:

B100 = 100% biodiesel
R100 = 100% renewable diesel
TGB = triglyceride blend (75% oil + 25% gasoline by volume)
RBD = refined, bleached, deodorized

Subscripts:

$_1$ = heavy blend
$_2$ = full boiling range

Table 2-3. Engine operating conditions during testing period.

Engine Parameter	Mean	Coefficient of Variance %	Engine Parameter	Mean	Coefficient of Variance %
Torque [N-m]	251	0.4	Jacketwater In Temp [C]	67.2	1.3
Power [kW]	44.8	0.5	Jacketwater Out Temp [C]	69.9	1.1
Speed [RPM]	1700	0.0	Engine Oil Temp [C]	90.6	0.2
BMEP [kPA)	703	0.0	Fuel Inlet Temp [C]	22.3	0.7
Fuel Supply Flow [g/min]	177	3.7	Fresh Air Temperature [C]	23.8	0.3
Throttle Position [%]	54.3	0.0	Inlet Air Temp [C]	35.1	1.0
Turbo Speed [RPM x 1000]	82.7	0.3	Manifold Air Temperature [C]	27.5	0.3
Start of Injection [°BTDC]	2.60	3.5	Compressor Inlet Air Temperature [C]	31.4	3.3
Intake Manifold Pressure [psig]	5.98	4.2	Charge Air Pre-IC Temp [C]	94.4	0.3
Exhaust Manifold Pressure [psig]	7.42	1.5	Charge Air Post-IC Temp [C]	22.2	0.5
Engine Oil Pressure [psig]	45.6	5.0	IC Water Inlet Temp [C]	12.9	0.1
Precooler Pressure [psig]	6.47	1.3	IC Water Outlet Temp [C]	15.6	0.2
Pre DPF Pressure [psig]	0.160	33.1	Pre DPF Temp [C]	350	0.2
Rail Pressure [psig]	17900	0.2	Post DPF Temp [C]	311	0.2

Table 2-4. Physical properties of test fuels.

FUEL TYPE	Density @ 20° C (g/cm3) *Anton Paar DSM5000*	Sound Velocity @ 20° C (m s-1) *Anton Paar DSM5000*	Kinematic Viscosity @ 40° C (mm2 s-1) *Anton Paar SVM3000*	Lower Heating Value J g^{-1} *IKA C200*
DIESEL	0.8414	1372.89	2.3411	45263
Carinata B100	0.8840	1427.49	5.7133	39665
Carinata TGB	0.8817	1413.68	12.852	40478
Carinata $R100_1$	0.8173	1351.23	1.8789	45126
Carinata $R100_2$	0.8175	1351.15	1.894	44611
Camelina B100	0.8877	1424.2	4.9297	38982
Camelina TGB	0.8811	1398.09	8.9612	39708
Camelina R100	0.7825	1359.79	3.4835	44911
Pennycress B100	0.8938	1437.69	7.4914	39631
Pennycress TGB	0.8797	1410.53	12.006	39789
Soybean B100 (crude)	0.8845	1417.06	4.7385	39451
Soybean B100 (RBD)	0.8858	1419.01	4.9638	39400
Soybean TGB (crude)	0.8744	1377.89	7.8246	39646
Soybean TGB (RBD)	0.8801	1396.42	9.407	40575
Corn B100 (RBD)	0.8924	1421.61	5.0825	39519
Corn TGB (RBD)	0.8795	1397.76	9.3253	41150
Corn TGB (crude)	0.8847	1419.42	8.3201	39629
Canola B100	0.8754	1391.28	6.3684	40459
Canola TGB	0.8946	1424.97	10.011	39666
Sunflower B100	0.8846	1406.31	5.4996	39838
Sunflower TGB	0.8750	1375.83	11.752	39672

Notes:

B100 = 100% biodiesel

R100 = 100% renewable diesel

TGB = triglyceride blend (75% oil + 25% gasoline by volume)

RBD = refined, bleached, deodorized

Subscripts:

$_1$ = heavy blend

$_2$ = full boiling range

2.3 Results and discussion

2.3.1 Brake specific fuel consumption results

Brake specific fuel consumption (bsfc) is a frequently used metric to describe engine efficiency. A low value for bsfc is desirable since at a given power level less fuel will be consumed. Figure 2-5 shows the bsfc for all fuels used in the evaluation grouped by fuel type. Error bars indicate the standard deviation in each run. For the petrodiesel runs, the graph indicates the median value of the three petroleum runs. The three petrodiesel runs had nearly

identical bsfc results, indicating low variability throughout the testing period and a valid comparison of feedstocks and fuel types.

The industrial oilseed derived fuels have very similar performance as compared to the traditional oilseeds. Average bsfc for the industrial oilseed biofuels was within ±1.3% of the conventional oilseed biofuels for each fuel pathway. Refinement level did not have a significant effect on bsfc. Only minor differences were observed between the crude and RBD runs for the two feedstocks tested.

Fuel pathway did have an effect on bsfc. The biodiesel run had a higher bsfc than the TGB run for every feedstock. The average bsfc for all biodiesel runs was 246.9 g/kW-hr while the average for TGB runs was 239.1 g/kW-hr, a 3.2% reduction. The renewable diesels had lower bsfc values than the other biofuel types, with results very similar to the petroleum runs. The three-run average for the R100 biofuels was 219.2 g/kW-hr and the three-run average for petrodiesel was 222.7 g/kW-hr. The bsfc results are related to the energy content differences of the test fuels shown in Table 2-4.

The bsfc results described above were for fuel flow measured on a mass flow basis. In practice, operators typically measure engine efficiency and fuel economy (fuel flow) on a volumetric basis – miles per gallon or gallons per hour. When taking in account the density differences of the fuel types, the biofuels generally had performance closer to that of petrodiesel than on a mass flow basis, due to their higher density. Several TGBs have a volumetric bsfc only slightly higher than petrodiesel fuel, with the mean value for all TGBs only 1.9% higher than the petroleum runs.

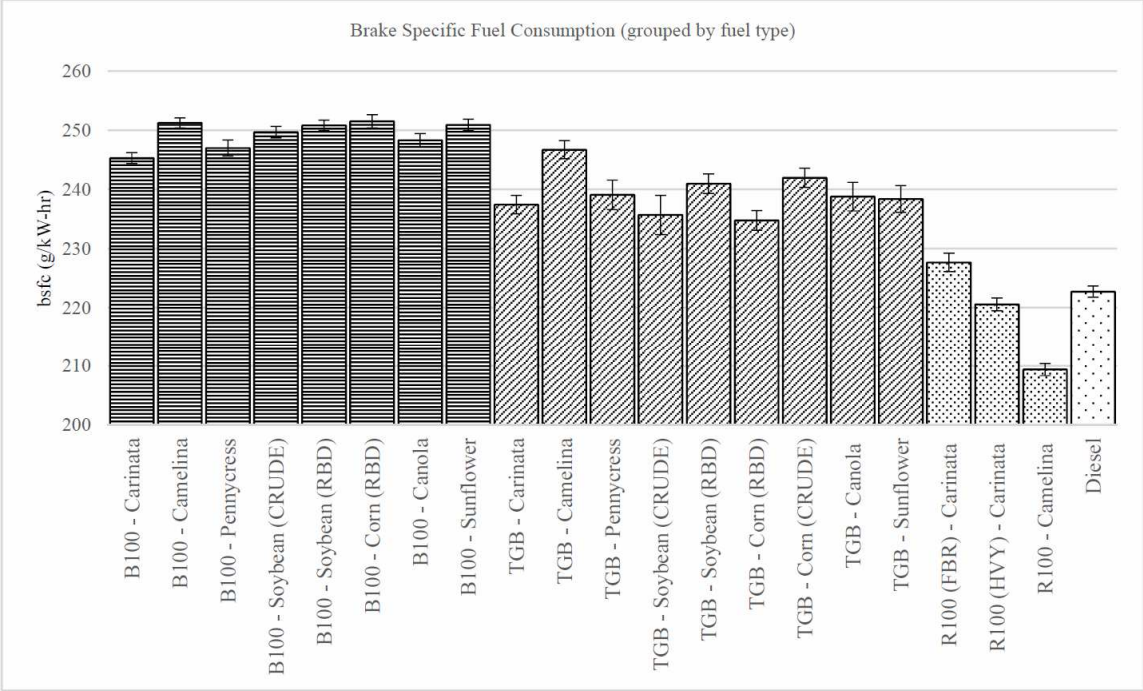

Figure 2-5. Brake specific fuel consumption (grouped by fuel type).

2.3.2 Brake thermal efficiency results

Brake thermal efficiency can be used to compare two engines if using the same fuel, or compare efficiency of an engine using multiple fuels. In general terms, thermal efficiency is how efficient an engine can convert the energy in the fuel into useful power. As shown in Figure 2-6, all biofuels had higher thermal efficiencies than petrodiesel. Error bars indicate the standard deviation in each run. For the petrodiesel runs, the graph indicates the median value of the three petroleum runs. The TGBs had a higher thermal efficiency than the B100 fuels for all seven feedstocks, with an average thermal efficiency 2% higher than petroleum. Other researchers have found biodiesel thermal efficiency similar to petroleum, or in some cases higher than petroleum especially at lower speeds [101]. The increased lubricity of the biofuels could cause a reduction in engine friction and improved efficiency at this load [101]. For the TGB fuels, the improvements in efficiency could also be tied to the improved spray patterns in combustion due to explosive vaporization of the low boiling constituents [80]. Additionally, since the heating

value of the biofuels is lower, more mass needs to be injected into the combustion chamber. At low load, this may be realized as improved jet penetration and air utilization.

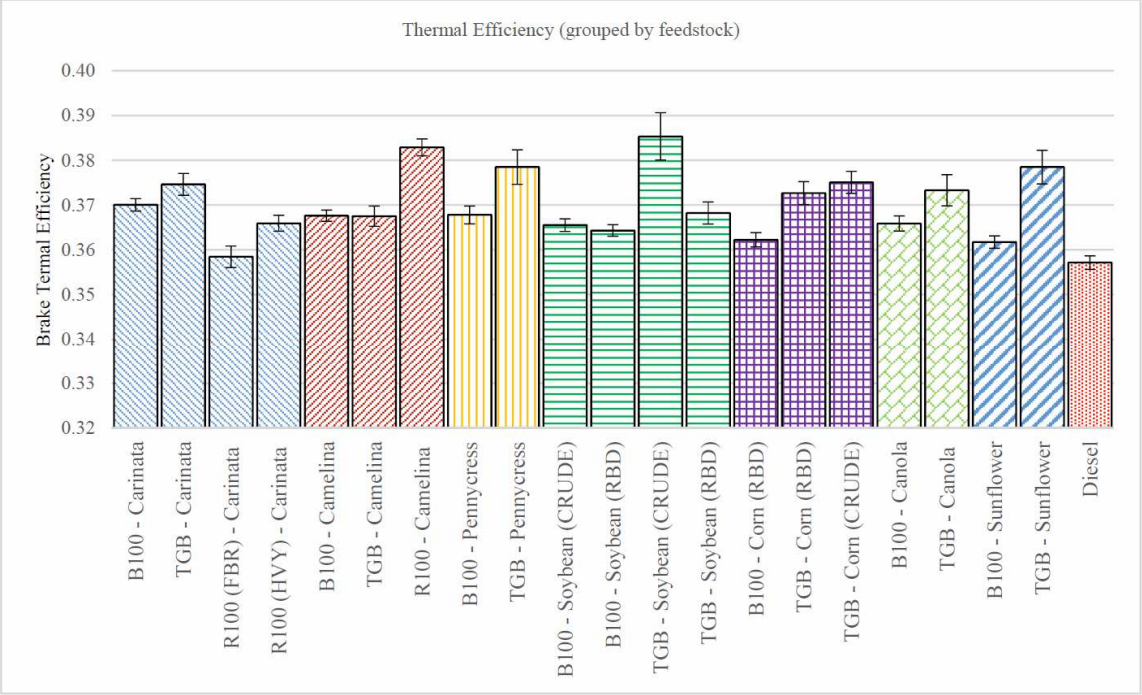

Figure 2-6. Brake thermal efficiency.

2.3.3 Brake specific emission results

Brake specific emissions (BSE) relate emission mass flow to engine loading. BSE takes into account different power levels and fuel composition. Biofuel feedstock type had minimal impact on emissions, indicating the industrial oilseeds had similar performance to the traditional feedstocks. Fuel pathway did have an effect on emissions.

The emissions of carbon monoxide for the engine testing are shown in Figure 2-7. The biodiesels had a reduction in CO emissions compared to petrodiesel, which is common for biodiesel use [133]. The renewable diesels also had slight reductions as compared to petroleum. The TGB biofuels had performance similar to petrodiesel for most runs. For all emission measurements, the graphs indicate the median value of the three petroleum runs with the high

and low values indicated by error bars. The errors bars indicate a small amount of variability in the three petrodiesel runs for CO measurements.

The emissions of oxides of nitrogen for the engine testing are shown in Figure 2-8. The biodiesels had a small increase in NO_x emissions compared to petrodiesel, which is common for biodiesel use [133]. The TGB and R100 biofuels had performance similar to petrodiesel, or slight reductions for some runs. In one of the few categories of emissions where petrodiesel typically outperforms biodiesel, the renewable diesel average was 6% lower for NO_x emissions than petroleum. The errors bars indicate a small amount of variability in the three petrodiesel runs.

The emissions of non-methane hydrocarbons (NMHC) for the engine testing are shown in Figure 2-9. The biodiesels had similar or slight decreases in NMHC emissions compared to petrodiesel. A decrease in NMHC emissions is common for biodiesel use, although emissions can vary with engine speed and load [133]. Some TGB biofuels had higher NMHC emissions than petrodiesel. The R100 biofuels had performance similar to petrodiesel. The errors bars indicate a higher amount of variability in the three petrodiesel runs as compared to other emission measurements. There was no trending with time of day, or other known factors, that may have contributed to this increased variability over other emission measurements.

The emissions of volatile organic compounds (VOCs) during the engine testing are shown in parts per million (ppm) in Figure 2-10. The EECL's FTIR groups VOCs as non-methane, non-ethane, and non-aldehydes hydrocarbons below C4. The biodiesels had a slight decrease compared to the other fuels. TGB and R100 emissions were similar to petrodiesel. VOCs can create photochemical smog under certain conditions, so it important that biofuels have similar or reduced VOC emissions as petrodiesel [134]. The emissions of formaldehyde (CH_20) during the engine testing are shown in ppm in Figure 2-11. B100 and R100 emissions were similar to

petrodiesel. The TGB biofuels had increased emissions of CH_20 as compared to the other fuels. The gasoline used as a blending agent for the TGB fuels contained 10% ethanol (E10). Ongoing TGB testing at the EECL will evaluate ethanol's contribution to formaldehyde and other emissions by sweeping ethanol in the blend from 0% to 85% (E85). Despite the increase for the TGBs, the overall levels were small, with all test runs less than 5 ppm. The remaining hydrocarbons measured by the FTIR were all small in concentration, and did not show significant differences between feedstocks or fuel pathways.

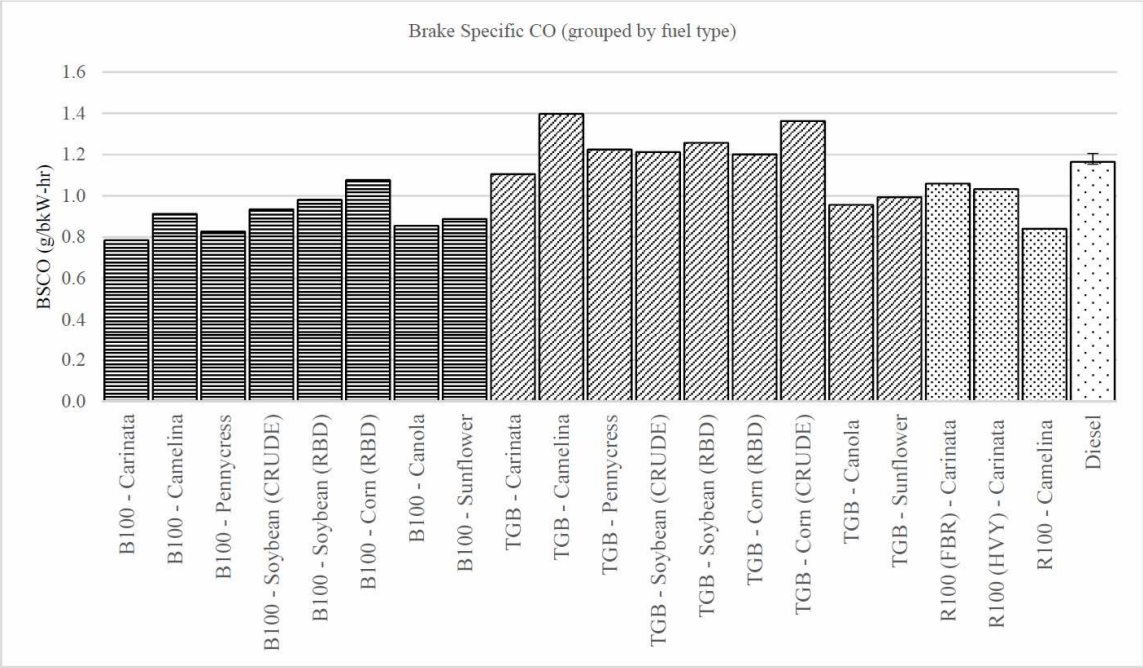

Figure 2-7. Brake specific carbon monoxide results.

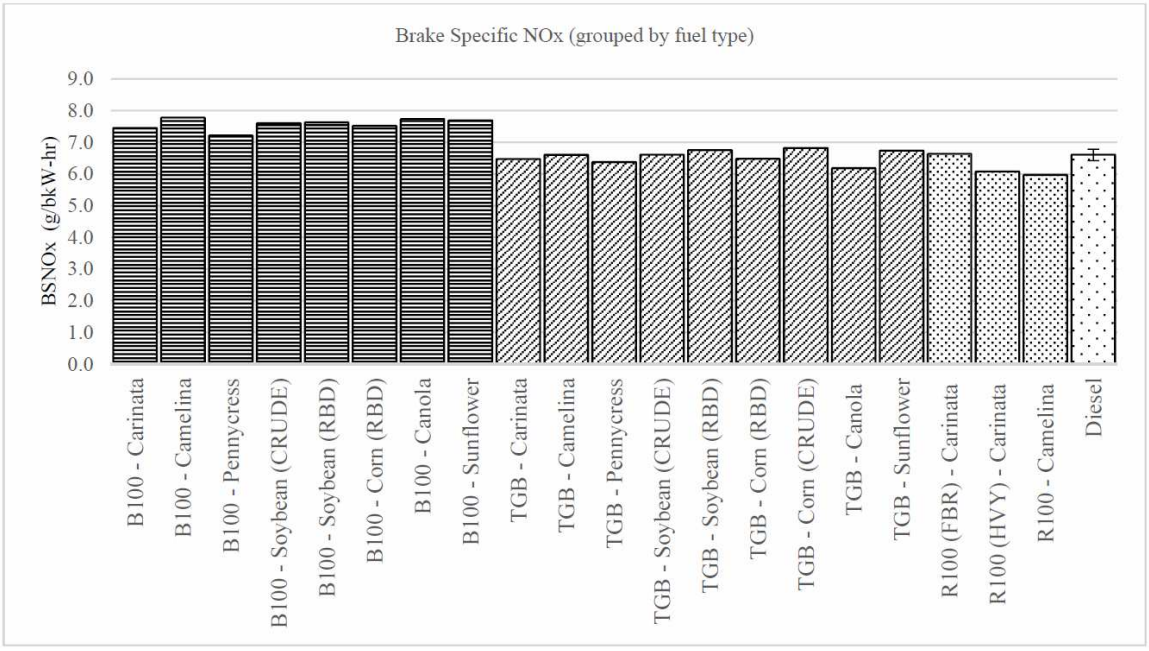

Figure 2-8. Brake specific oxides of nitrogen (NO_x) results.

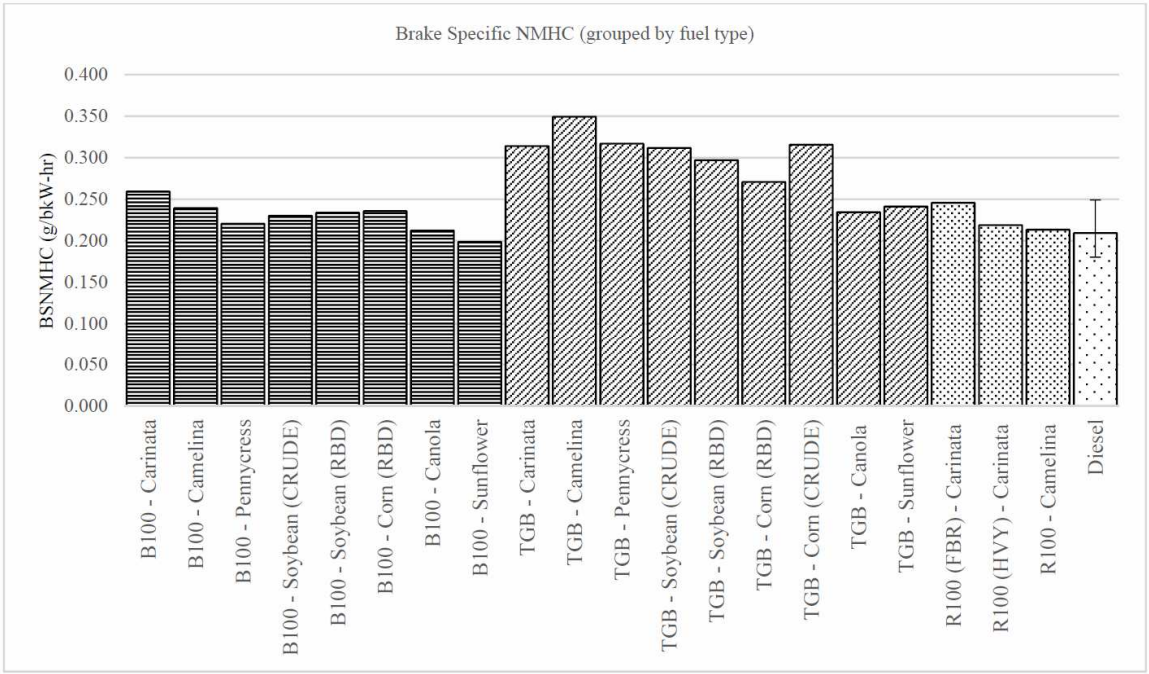

Figure 2-9. Brake specific non-methane hydrocarbon results.

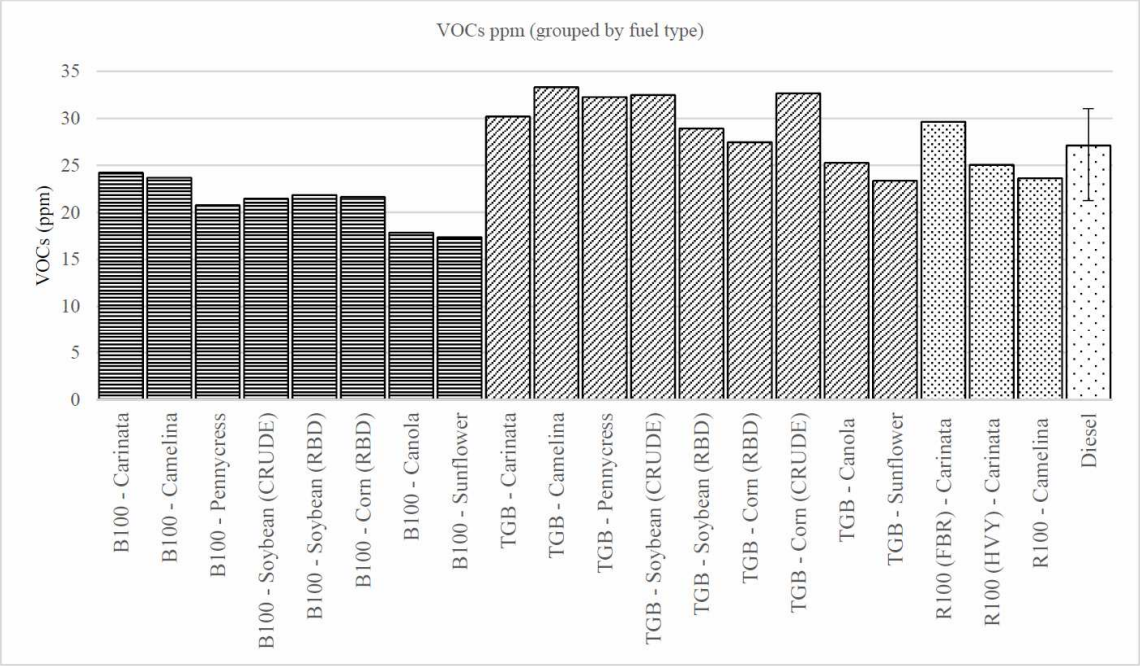

Figure 2-10. Emissions of volatile organic compounds.

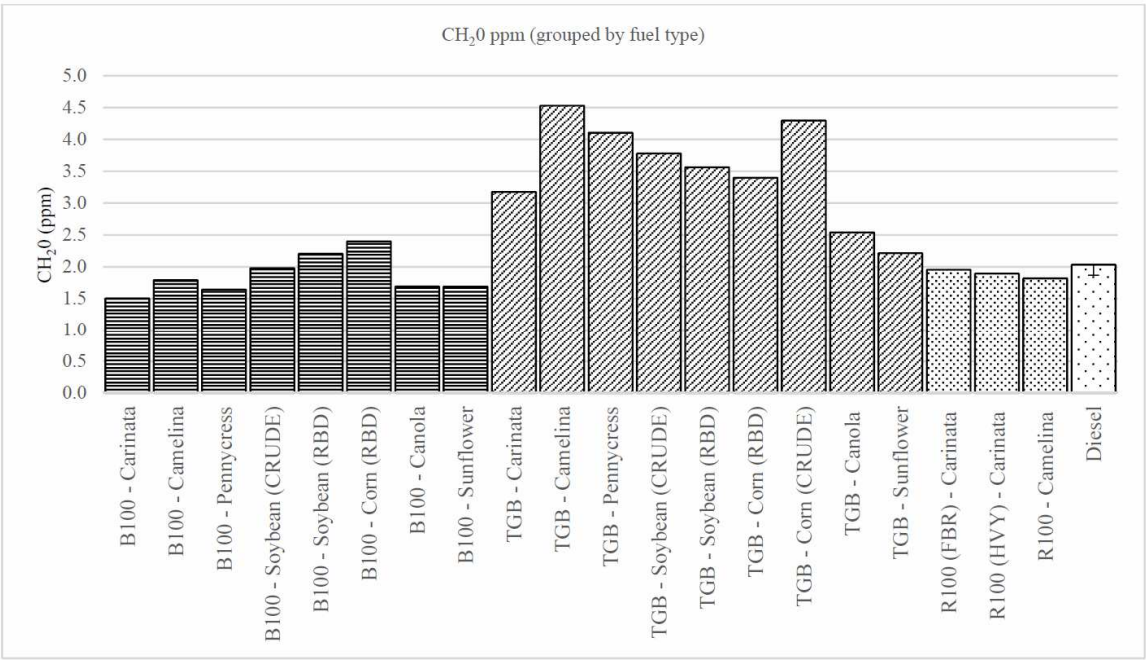

Figure 2-11. Emissions of formaldehyde.

2.3.4 Particulate matter results

Particulate matter (PM) measurements included total mass emissions (g/hr), elemental carbon (EC) to organic carbon (OC) ratio, and particle size distribution using a scanning mobility

particle sizer (SMPS). Total PM mass emissions were measured gravimetrically via collection onto Teflon filters. The resulting brake specific particulate matter results are shown in Figure 2-12. At this engine load and speed, most biofuels had PM emissions slightly higher than petrodiesel. Typically, biofuels use shows a reduction in PM emissions [133]. Due to limited feedstock availability, data collection was limited to 5 min points and the resulting PM collected was near the limit of quantification (LOQ) for each run. Increased run times during future testing will increase the understanding of PM emission from these feedstocks and fuel pathways. PM emissions can also change with engine operating parameters; further study using additional engine operating points would also give a better comparison of feedstock and fuel types with respect to PM emissions.

Elemental carbon (EC) and organic carbon (OC) were measured via collection on quartz filters, which were subsequently analyzed using a Sunset Labs OC/EC Analyzer. Unfortunately, due to the small amount of PM collected on the quartz filters during each run, all the measurements were above the LOQ.

A Grimm Technologies Sequential Mobility Particle Sizer (SMPS) was used to measure particle size distributions from 10 to 1000 nm – note that in the subsequent figure, the distribution is only shown to 100 nm for increased resolution. In general, each fuel feedstock and type produced trends in size and distribution that were similar to petroleum. Figure 2-13 shows the results for soybean biofuels. There was no significant difference in crude and refined fuel particle results for the soybean biodiesel runs, but a small reduction in peak particle count for the RBD TGB run.

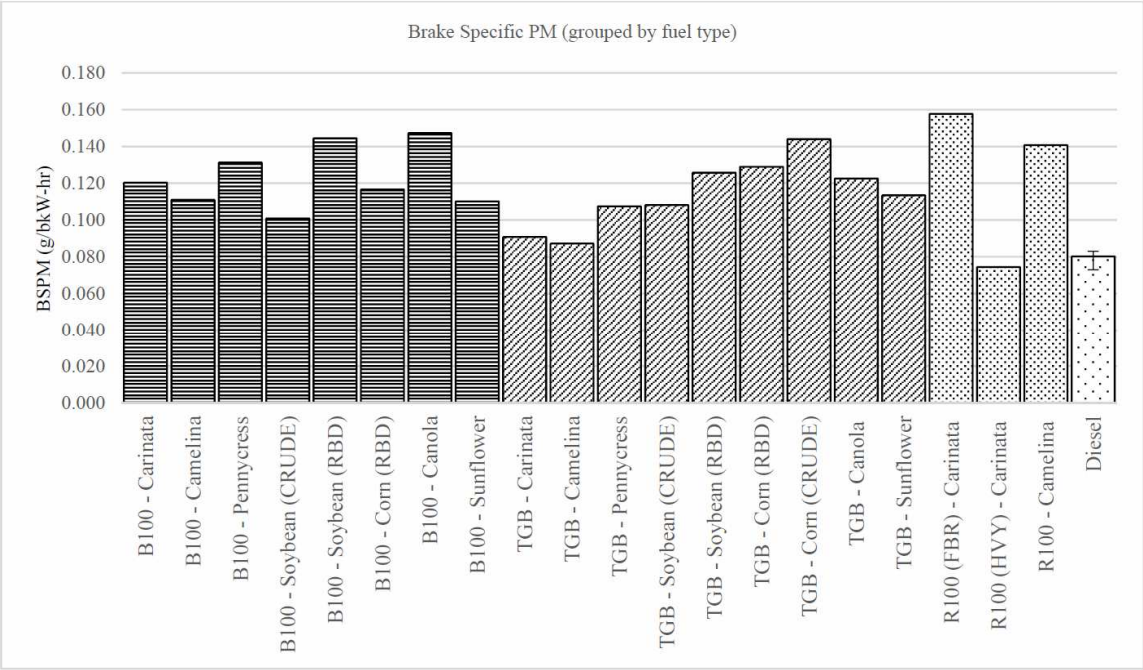

Figure 2-12. Brake specific particulate matter.

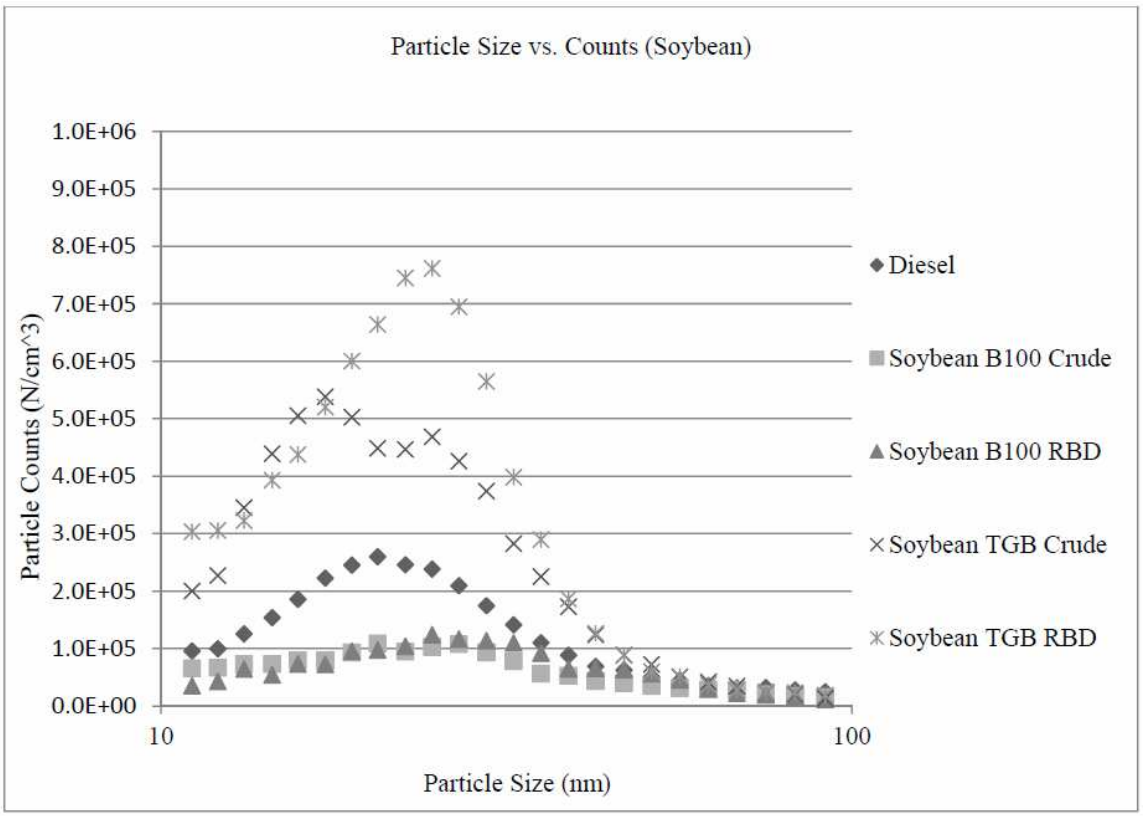

Figure 2-13. Particle size versus counts – soybean feedstock.

2.3.5 Heat release results

A high-speed pressure transducer was installed in the glow plug port of cylinder 1 as described in Section 2.2.2. The in-cylinder high-speed pressure data can be plotted as a function of crank angle. The known geometry of the cylinder and connecting rod can then be used to calculate the cylinder volume as a function of crank angle. Pressure versus volume curves can then be used to calculate the apparent rate of heat release (J/deg) due to fuel combustion in the cylinder. A low pass Inverse Chebyshev filter was used to filter the oscillations due to the time derivative of pressure in the heat release curves.

Standard injection timing for this engine was used during testing. Except during startup, the John Deere 4045 test engine uses a single injection event. The engine ECU uses a lookup table based on throttle position, engine speed, and engine temperatures to determine injection timing. Even though the same engine speed and torque set points were used for each run, there were small injection timing differences due to differences in physical properties of fuels [135] and small fluctuations in operating conditions. The injection timing averages for each fuel type are shown in Table 2-5. The R100 runs had injection timing similar to petrodiesel. The B100 and TGB biofuels both had slight injection delays of 0.70° and 0.92° respectively.

The heat release curves of the biofuels were similar to petrodiesel with a few differences. Figure 2-14 shows the results for carinata biofuels, as compared to petrodiesel. The peak of the heat release profile is slightly smaller for the biofuels. Reductions in the peak rates of heat release were expected due to the lower energy contents of the biofuels [136]. The B100 and TGB heat releases are very similar. The renewable diesel peak is more similar in peak and shape to petroleum than the other biofuels. The heat release curves for the soybean biofuels as compared to petrodiesel are shown in Figure 2-15. The trends in fuel type are similar to the carinata results

in Figure 2-14. The refinement level of the vegetable oil feedstock did not have a significant effect on the heat release curves. The crude and RBD results were very similar.

The location of 10% mass fraction burn duration is shown in Figure 2-16. The test engine was insensitive to fuel type, with similar results for each fuel pathway. The 50% and 10–90% burn duration were also analyzed, and similarly did not show major differences between fuel pathway or feedstock.

Table 2-5. Injection timing of test fuels.

	Injection Timing	
Fuel Type	Average (°BTDC)	Coefficient of Variance (%)
Diesel	3.195	2.70
R100	3.259	2.83
B100	2.492	5.12
TGB	2.272	5.55

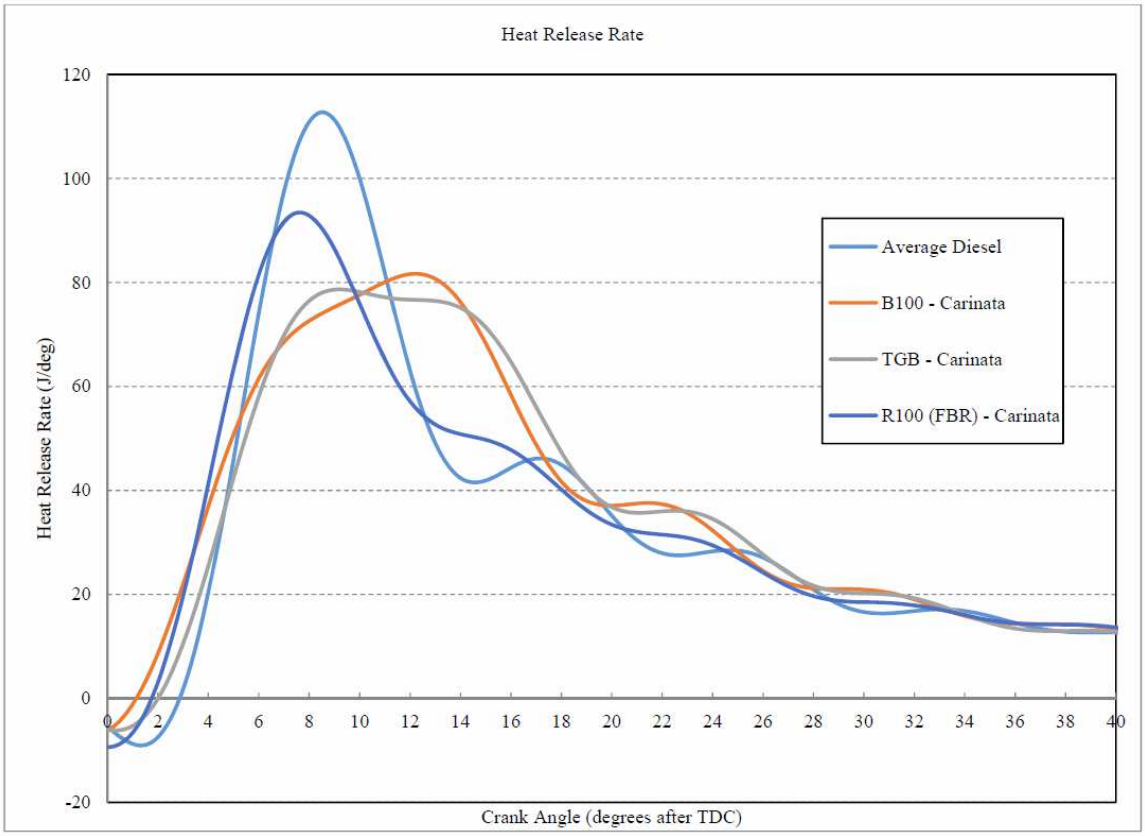

Figure 2-14. Heat release of carinata biofuels.

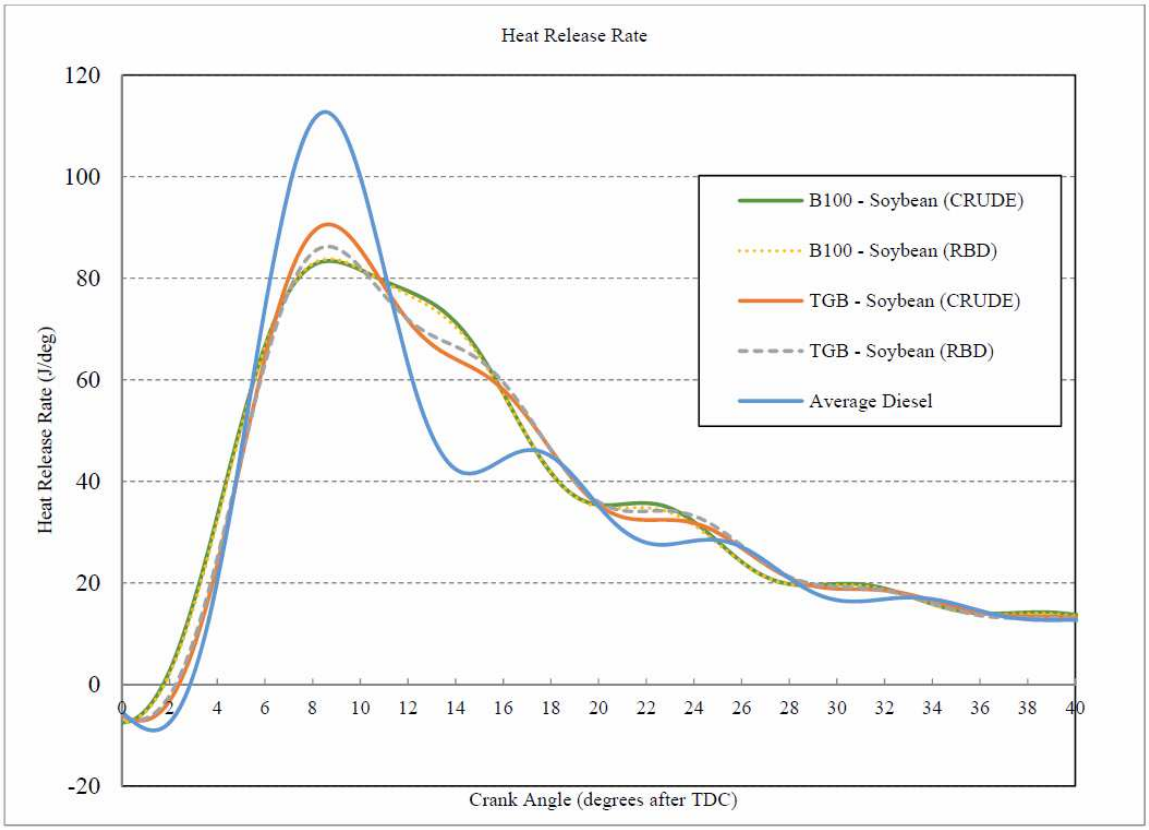

Figure 2-15. Heat release of soybean biofuels.

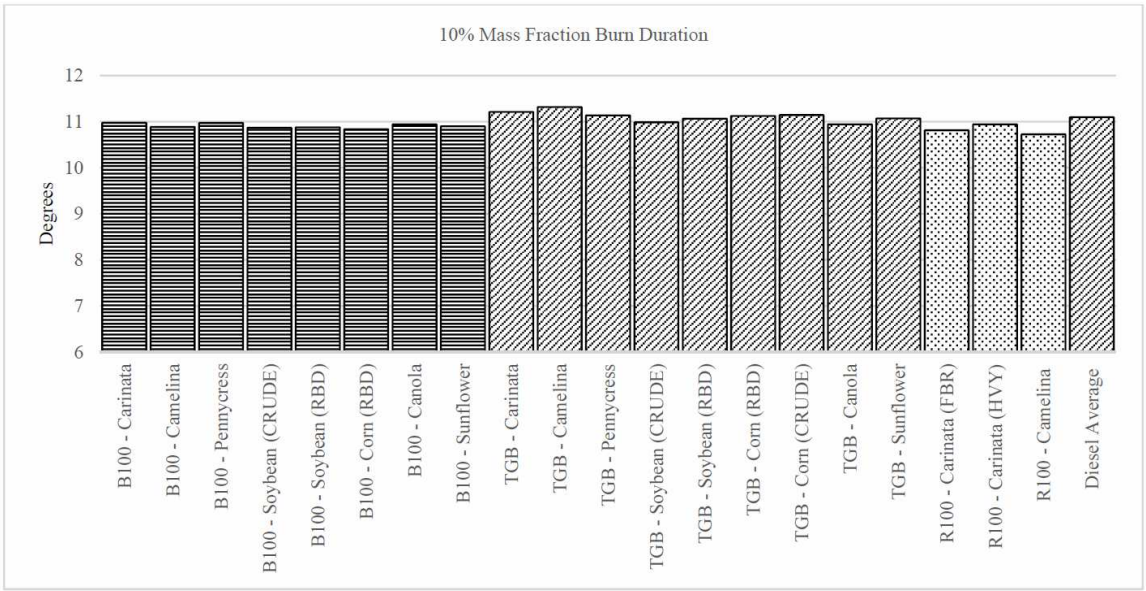

Figure 2-16. 10% mass fraction burn duration for test fuels.

2.4 Conclusions

Industrial oilseeds camelina, carinata, and pennycress had very similar engine performance to the traditional oils in this evaluation. Fuel consumption, thermal efficiency, and emissions were all were typical as compared to traditional oilseed feedstocks. For example, average bsfc for the industrial oilseed biofuels was within ±1.3% of the conventional oilseed biofuels for each fuel type. A recent camelina biodiesel conversion study found camelina biodiesel did not meet ASTM D6751 standards for cetane number, distillation temperature, and oxidation stability, which was suggested as serious drawbacks for camelina as a biodiesel feedstock [51]. However, this engine performance study found no engine operability, performance, or emissions issues when using camelina fuels or significant differences from the other feedstocks. Durability testing would better quantify engine performance of using camelina biodiesel in the long term.

Fuel pathway did have small impacts on engine performance. The engine performance of TGBs was of special interest since they are easy to produce and inexpensive in farm-scale scenarios. Overall engine performance was favorable in all categories tested. TGBs had lower fuel consumption and a higher thermal efficiency than biodiesel for each feedstock tested. For several performance categories, TGB performed similar to petrodiesel. For example, the mean value for TGBs volumetric bsfc was only 1.9% higher than the petroleum runs. TGB combustion characteristics were similar to biodiesel. Initial research with TGBs indicates it may be an ideal candidate for farm-scale fuel production, which will bridge the gap for these industrial oils until the commercial market matures. The farm-scale fuel production procedures (i.e. crude oil, no pretreatments) did not negatively affect engine performance or emissions in a modern Tier 3 CI engine. Besides the on-farm use, TGBs may also be an ideal fuel pathway for using locally

produced plant oils worldwide in other niche markets, such as rural areas or in developing nations.

Biodiesel is also a viable fuel pathway for farm-scale scenarios. Biodiesel use offers several emission benefits. Biodiesel runs had reductions in CO, NMHC, VOC, and CH_20 emissions as compared to TGB runs. Biodiesel performance is much better understood than TGBs during long-term use. Most engine manufactures also certify their engines biodiesel compatible, which may be a major factor for farmers using modern equipment under warranty when choosing between biodiesel and TGB options.

The renewable diesels in the evaluation had performance as good as or better than petrodiesel in nearly category. These fuels are intended as ‘‘drop-in’’ alternatives, and this study shows they meet their goal. The renewable diesels offer petroleum-like engine performance and combustion characteristics, while still maintaining some of the benefits of biodiesel such as reduced CO emissions. NO_x emissions were also 6% lower for renewable diesel runs than petroleum.

Additional studies should focus on investigating TGB fuel properties for multiple blend ratios. In this study a 75% vegetable oil to 25% gasoline volumetric ratio, which was compatible with a modern CI engine without modification, was used. An extensive fuel property evaluation should be used to indicate how important fuel properties like density, viscosity, flash point and cold flow characteristics change with TGB blend ratio. Future engine testing at the EECL should involve changing ethanol content in the gasoline, to quantify ethanol’s effect on engine performance. While the initial engine performance testing was favorable, on-going long-term durability testing at the EECL should assess the impact of using TGBs in the combustion chamber, fuel system, and after-treatment components as compared to using SVO, biodiesel, and petrodiesel fuels.

Chapter 3. FUEL PROPERTY QUANTIFICATION OF TRIGLYCERIDE BLENDS WITH AN EMPHASIS ON INDUSTRIAL OILSEEDS CAMELINA, CARINATA, AND PENNYCRESS[2]

3.1 Introduction

3.1.1 Industrial oilseed's role in a constrained agronomic environment

Industrial oilseeds camelina (*Camelina sativa* L.), carinata (*Brassica carinata*), and pennycress (*Thlaspi arvense* L.) are alternative non-food oilseeds which have great potential to increase biofuel use and reduce cost. The positive agronomic attributes of these oilseeds allow them to fit into cropping systems and rotations that increase biofuel production on existing lands [137]. One example is fitting into the wheat-fallow rotation common in the Western U.S. Due to their short growing season and low water demands, camelina and carinata could be grown during this normally fallow period. Instead of a fallow period, an oilseed offers growers additional revenue from the energy crop as well as increased weed control, decreased soil erosion, carbon sequestration, disruption of undesirable pest cycles, and other benefits for the follow-on crop [138].

Oilseeds may also play an important role in the future of agriculture in areas that face harsh growing conditions. Industrial oilseeds have shown reduced water demand compared to traditional oilseed crops in some scenarios [45]. For example, agronomic trials have found camelina is better able to compensate for early water deficits [139] and has less aggressive soil water extraction than some traditional oilseeds [140]. Another benefit is fall planted and spring harvested oilseeds have peak water needs during a traditionally low water demand period [141]. Finally, these industrial oilseeds may also work well in fields that are under water leasing

[2] Manuscript published in *Fuel* 153 (2015) 19–30 by A.C. Drenth et al. [179]

arrangements. This arrangement may be especially important to Colorado and other regions with water constraints. More than 80% of Colorado's 5.2 million population lives in the 12 county region of the Front Range [142]. The population growth in this region has been higher than the national average for over 20 years, with projected population to nearly double between year 2000 and 2040 [143]. Population growth can create a struggle for water between agriculture and municipal uses. Rotational fallowing or other water leasing arrangements are alternatives that would allow water resource availability for municipal use while still sustaining agricultural production. For example, this type of ag/urban water sharing agreement is under study in Colorado's Arkansas River Basin and would provide an estimated 9,100 acre-feet of water annually by 2050 [144].

Despite the promise of these industrial oilseeds, the commercial market for them is still maturing. For example, it was recently estimated camelina is only grown on ~1% of the wheat-fallow acreage it is well suited for, with 95% of camelina oil production used in biofuel test programs [145]. Until the commercial market matures, the use of these oilseeds to produce on-farm fuel may be the only viable market in some areas. Recent studies have found the economics for farm-scale fuel production can be favorable in some scenarios [92], [112]. The quantity of fuel used on farms is significant; in some Midwestern U.S. states farm use of distillate fuel represents more than 20% of total consumption [146].

3.1.2 Fuel pathways for vegetable oil

Due to the great potential of oilseeds camelina, carinata, and pennycress in this region, the Engines and Energy Conversion Laboratory (EECL) at CSU recently completed a compression ignition engine (diesel engine) performance and emission evaluation of these feedstocks using multiple biofuel pathways [137]. The objective of the study reported herein is to build on the

engine testing results with a comprehensive evaluation of several fuel properties for these promising oilseeds, including three industrial oilseeds (camelina, carinata, pennycress) and four conventional (soybean, canola, sunflower, corn) biofuel feedstocks. Fuel property evaluation compared the more traditional biofuel pathways of straight vegetable oil (SVO), biodiesel (B100), and renewable diesel (R100) [116], [130] with the less known triglyceride blends (TGB) pathway. A triglyceride-blend (TGB) is formed when SVO is mixed with another less viscous fuel (other than petrodiesel), and the resulting solution used as a petrodiesel substitute [137]. E10 gasoline was used to form the TGBs in this study unless otherwise noted. Peer reviewed literature found on this type of blend is extremely limited, although several U.S. farmers have been successfully using SVO–gasoline blends for several years [97]. Using E10 gasoline as a blending agent has several benefits: it is readily available, has high energy content, inexpensive, and has shown complete miscibility and stability with SVO during EECL testing. Like other blends/emulsions of this nature, as compared to biodiesel, producing TGBs is fast, requires low energy inputs, does not create waste products, and does not require a catalyst [94], [137]. They can be splash blended, and do not need changes in temperature, pressure, or large amounts of agitation to form a solution. TGBs change the physical properties of SVO to be more similar to petrodiesel; the recent engine testing at the EECL has found this type of blend compatible with modern direct injection (DI) engines without modification [137]. Fuel property evaluations for these industrial oilseed feedstocks have been completed for the biodiesel (B100) fuel pathway [49], [51], [53], [65], but not for the R100 and TGB pathways. TGB fuel property data has also not been reported for the conventional oils of this study. This research explores how several key fuel properties of industrial oilseeds compare to conventional biofuel feedstocks. There is no ASTM standard for TGB fuels, so the results of the properties tested are directly compared to

petrodiesel and to the other renewable fuel pathways. Previously mentioned engine testing used TGBs formed using a 75% SVO to 25% E10 gasoline volumetric ratio. The fuel property study also explored how other blend ratios affect fuel properties.

3.2 Materials and methods

3.2.1 Test fuel preparation

Oil extraction and fuel preparation methodologies for SVO, B100, and TGB fuels were kept consistent with typical farm-scale fuel procedures. Since most farm-scale producers do not have access to large scale refining, crude (unrefined) vegetable oil was used as the biofuel feedstock unless otherwise noted. To evaluate the effect of oil feedstock refinement on fuel properties, biofuels produced from both crude and refined, bleached, and deodorized (RBD) soybean and corn oil were used in testing. The sources of oil and other testing materials are shown in Table 3-1.

The TGBs used in the evaluation were formed by initially filtering the SVO with a 10 μm polypropylene filter, then blending with E10 gasoline at various volumetric ratios. The resulting TGB was transferred to a high-density polyethylene (HDPE) container, and then agitated by manually shaking the container for ~30 s to ensure adequate mixing before filtering again to 1 μm.

Biodiesel is defined by ASTM as fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [100]. For this study, SVO was converted to biodiesel (B100) via transesterification (alcoholysis) in a research-scale reactor in the EECL. Vegetable oil was added to the reactor, recirculated, and heated to 60 °C. In a separate container, methoxide was prepared from methanol and potassium hydroxide (KOH) at a 1:5 molar ratio and 1 wt. % KOH. After adding the methoxide to the oil, the mixture was recirculated for two hours

to promote the conversion to fatty acid methyl esters. Following the reaction and settling, the lower glycerol layer was separated. The biodiesel was then water washed until a neutral pH was obtained, air dried, and filtered to 1 μm.

Renewable diesel is a non-ester renewable fuel that is pure hydrocarbons and indistinguishable from petrodiesel but made from biomass [130]. Applied Research Associates (ARA) and Chevron Corporation provided the renewable diesels (R100) in this evaluation. ARA provided two variations of Renewable, Aromatic, Drop-in Diesel (ReadiDiesel). ReadiDiesel is produced using the Biofuels ISOCONVERSION (BIC) process, which combines ARA's Catalytic Hydrothermolysis (CH) process and Chevron Lummus Global's (CLG) hydroprocessing technology. One ReadiDiesel sample was described as their ''heavy blend'' and is intended to meet the Navy Distillate Diesel Fuel specification (NATO symbol F-76). The other sample was described as their ''full boiling range'' fuel, and is intended as a drop-in, #2 petrodiesel substitute. Both were produced using carinata oil as feedstock. Chevron Corporation labeled their renewable diesel as ''experimental hydrotreated renewable diesel'', which was produced from camelina oil. Hydrotreating of vegetable oils and the catalytic hydrothermolysis process is described in other publications [130].

Table 3-1. Source of testing materials.

MATERIAL	SOURCE	LOCATION
Carinata Oil	Agrisoma Bioscience, Inc.	Saskatoon, SK, Canada
Camelina Oil	ClearSkies, Inc.	Bozeman, MT, USA
Pennycress Oil	Arvens Technology, Inc.	Peoria, IL, USA
Soybean Oil	South Dakota Soybean Processors, LLC	Volga, SD, USA
Corn Oil	Glacial Lakes Energy	Watertown, SD, USA
Canola Oil	Painted Rock Farms	Stratton, CO, USA
Sunflower Oil	Prairie View Farms	Penokee, KS, USA
Carinata R100	Applied Research Associates, Inc.	Panama City, FL, USA
Camelina R100	Chevron Corporation	Richmond, CA, USA
Diesel Fuel, Grade No. 2-D S15	Team Petroleum, LLC	Fort Collins, CO, USA
Ethanol, ACS/USP Grade	Pharmco-Aaper	Brookfield, CT, USA
E0 Gasoline, 87 octane	Hill Sinclair	Greeley, CO, USA
E10 Gasoline, 87 octane	Agfinity Cooperative	Eaton, CO, USA

3.2.2 Fuel property test runs

Biofuels should have similar physical properties to the petroleum fuels they intend to replace. Several important fuel properties were measured for all test fuels. Seven feedstocks were evaluated, using four fuel pathways, and for two refinement levels as shown in Table 3-2.

To test how the blend ratio of SVO to E10 gasoline affects TGB fuel properties, a blend sweep of the three industrial oilseeds and one traditional oilseed (canola) was also performed for some of the physical properties for the following SVO to E10 volumetric ratios: 95/5, 85/15, 75/25, 65/35, 55/45. Blends of SVO and petrodiesel, or dilution mixtures, have also been researched for some oilseeds [93]. This fuel option was not included in the engine performance study, but was included in this fuel property evaluation to compare E10 gasoline and petrodiesel as blending agents for SVO. Canola oil was also blended with petrodiesel at the same five ratios to determine how fuel properties compare to blending canola SVO and E10.

Table 3-2. Fuel property evaluation test runs.

FUEL PATHWAY EVALUATED	FEEDSTOCK TYPE	REFINEMENT LEVEL
DIESEL	*Petroleum*	
SVO , B100 , TGB , R100$_a$	Carinata	Crude
SVO , B100 , TGB , R100	Camelina	Crude
SVO , B100 , TGB	Pennycress	Crude
SVO , B100 , TGB	Soybean	Crude & RBD
SVO , B100 , TGB	Corn	Crude & RBD
SVO , B100 , TGB	Canola	Crude
SVO , B100 , TGB	Sunflower	Crude

Notes:
B100 = 100% biodiesel
R100 = 100% renewable diesel
TGB = triglyceride blend (75% oil + 25% E10 gasoline by volume)
SVO = straight vegetable oil
RBD = refined, bleached, deodorized

Subscripts:
$_a$ = both heavy and full boiling range blends were tested

3.2.3 Fuel property test methods

An Anton Paar SVM3000 Viscometer was used to measure viscosity of the test fuels of Table 3-2 and blend sweeps in accordance with ASTM test method D445. Viscosity is a very important quality of fuel. A high viscosity, often thought of as fluid thickness, will result in

increased wear or malfunction of engine components. High viscosity fuels have been linked to incomplete combustion that in turn causes ring sticking and engine deposits [93]. Reducing viscosity to levels suitable for engine use is the primary reason vegetable oil is converted to biodiesel through transesterification or reduced through another fuel pathway [93], [103].

The density and speed of sound of the test fuels of Table 3-2 and blend sweeps was determined by an Anton Paar DSM5000 in accordance with ASTM D4052. It is important petrodiesel substitutes have similar density and speed of sound to petrodiesel for compatibility with the engine fuel system.

A Petrolab 12-1771 Automatic Flashpoint Tester was used to determine flashpoint of the test fuels of Table 3-2 in accordance with ASTM D93. The flash point specification is not directly related to engine performance, but of importance in connection with legal requirements and safety precautions involved in fuel handling and storage [100].

Energy content of the test fuels of Table 3-2 was determined by an IKA C200 bomb calorimeter in accordance with ASTM D240. IKA C 723 benzoic acid calibration pellets were used to verify the calibration of the calorimeter. All calibration runs had errors less than 1%. IKA C 9 gelatin capsules were used to contain the test fuel to prevent any volatility loss of fuel during the calorimeter testing prior to ignition. Calorific values were also obtained for a blend sweep of carinata TGB.

Cold Filter Plugging Point (CFPP) was measured for the test fuels of Table 3-2 and blend sweeps in accordance to ASTM D6371 using a Lawler Manufacturing Company's Automatic Cold Flow Property Tester to give an indication of cold weather performance. The CFPP of a fuel provides an estimate of the low temperature vehicle operability [147], and gives a relative comparison of cold weather performance for all test fuels.

TGB lubricity has not previously been tested. To evaluate TGB lubricity, a High Frequency Reciprocating Rig (HFRR) test was performed in accordance with ASTM D6079 (60 °C) and compared to published data. A 75% crude soybean oil + 25% E10 gasoline based TGB was used in the HFRR. Soybean oil was used as the feedstock since more published data was available for comparison than the industrial oils in this study. A PCS Instruments (London, UK) Model HFRHCA8 HFRR lubricity tester was used to evaluate TGB lubricity. At the conclusion of each test, the ball was visually inspected for wear and the dimensions of an observed wear scar (μm) on the ball were averaged. All wear scar data are the averages of two replicates. A summary of the fuel property test methods is shown in Table 3-3.

Table 3-3. Fuel property test methods.

FUEL PROPERTY	MEASUREMENT INSTRUMENT	METHOD
Viscosity	Anton Paar SVM3000	ASTM D445
Density	Anton Paar DSM5000	ASTM D4052
Speed of sound	Anton Paar DSM5000	ASTM D4052
Heating value	IKA C200	ASTM D240
Flashpoint	Petrolab 12-1771	ASTM D93
Cold Filter Plugging Point	Lawler DR4-14	ASTM D6371
Lubricity	PCS Instruments HFRHCA8	ASTM D6079

3.2.4 Test methods to evaluate the physical and chemical stability of TGBs

TGBs (mixtures of SVO, gasoline, and ethanol) must be homogenous and stable to be considered a viable petrodiesel substitute. If a blend of the three components were to separate during storage or in the engine fuel system, it could cause damage to engine components. The previously mentioned engine tests and fuel property tests in this paper all used E10 as a blending agent, which has shown complete solubility with SVO during storage and previous engine testing. The gasoline acts as a co-solvent for the blend to solubilize the otherwise nearly immiscible vegetable oil–alcohol (ethanol) mixture into a single-layer (isotropic) solution [94]. This study explored solubility of TGBs at several ratios of the three components to determine if higher levels of ethanol could be used. TGBs are a way to use ethanol in a diesel engine. Other

researchers have found ethanol blends can reduce engine emissions in some cases [148]. Blender pumps, now available at many locations in the U.S., would allow TGB users to easily select the amount of ethanol in their gasoline at the pump.

The solubility of the three-component blend was tested using phase diagrams. The volumetric content of SVO to gasoline to ethanol was varied in 10% increments using an Eppendorf Reference pipette. Certified ethanol free gasoline (E0) was used as well as 99% purity ethanol. Anhydrous ethanol was used as a starting point, with 1% distilled water by mass added to precisely control water content. This water content corresponds with the maximum allowed by ASTM standard for ethanol fuel blends [149]. The resulting blend was stored in Chase Scientific screw thread glass culture tubes and shaken until thoroughly mixed. The tubes were left motionless for 10 days at room temperature and then visually inspected for separation. Diagrams were constructed for industrial oilseeds camelina, carinata, and pennycress, and traditional oil canola. This procedure was then repeated at a reduced (0 °C) and elevated (40 °C) temperature to simulate temperature ranges that could occur during fuel storage or during engine operation.

In addition to the phase (physical) stability of TGBs, the chemical stability of the fuel was tested to ensure no degradation of the blends over the expected timescale of use. Users of diesel fuels should strive to minimize storage, with ASTM defining long-term storage of biodiesel as greater than 6 months [100] and petrodiesel fuel as greater than 12 months [147]. Chemical reactions in TGBs could cause the formation of gums or sediments and plug filters or cause damage to the fuel injectors. Visual inspection of TGB samples stored for one year at the EECL did not reveal any sediments or separation. ^{1}H Nuclear magnetic resonance (NMR) spectroscopy was selected as an analysis tool to determine if there were any chemical changes or degradation in the components that were not visual. ^{1}H NMR has been used by others as an analytic tool to

determine vegetable oil quality and origin [150] and as a biodiesel production monitoring mechanism [151]. ^{1}H NMR has also been used to determine the concentration measurement of aromatic, olefinic and aliphatic fractions in gasoline samples [152]. The primary goal for this NMR testing was to determine if making TGBs (mixing SVO + E10 gasoline) can cause any chemical changes in any of the blend components, or if they remain only physically bonded when in solution.

To test the chemical stability, TGBs were formed from carinata oil and E10 gasoline. Five volumetric vegetable oil to E10 ratios (v/v) of TGBs were used in NMR testing including 95/5, 85/15, 75/25, 65/35, and 55/45. Approximately 24 h after the blends were mixed, 75 µL of the blends were dissolved in 675 µL deuterated chloroform. ^{1}H NMR spectra were collected on a 500 MHz Varian Inova (Santa Clara, CA) NMR spectrometer equipped with VJ-4.x software and using a 5 mm broadband probe. The following parameters were used: 5.477 µs 90 pulse lengths, 8003 Hz spectral widths, 32 transients with 32 k data points and 30 s relaxation delays. Chemical shifts were referenced in parts per million (ppm) relative to the signal of chloroform at 7.26 ppm. Carinata SVO and E10 were also analyzed by themselves to determine a baseline of each blend component. Finally, carinata biodiesel (B100) and carinata renewable diesel (R100) samples were also used in the analysis.

3.3 Results and discussion

3.3.1 Solubility and stability of triglyceride blends

The results of the TGB solubility testing described in the previous section are shown for carinata in Figure 3-1. The oil type had a small effect on solubility, but the general trends were the same for each feedstock. The results show ethanol content in the gasoline (higher E#) can induce phase separation in TGBs due to the differences in chemical structure of the oil and

alcohol [94], [148], [153]. The E# by TGB phase position is ethanol %/{ethanol % + gasoline %} by volume. For example, the TGB on the second row from the bottom, fifth from the left is formed by mixing 50% SVO, 10% ethanol, and 40% gasoline; the E# of this blend is E20.

Previous engine testing of TGBs used E10 gasoline since most of the U.S. fuel supply now contains 10% ethanol. Based on our results, we recommend users of TGBs to limit ethanol content in the gasoline–ethanol portion of the blend to 10% (E10) to ensure no TGB phase separation over a wide temperature range. Both elevated and reduced temperatures induced further phase separation as compared to room temperature. At the lower temperature, some TGBs with high vegetable oil content began to crystalize or gel.

Previous research using blends of petrodiesel, biodiesel, and ethanol found water content in the ethanol has a significant effect on blend solubility [148]. During that study, the three-component blend was completely soluble across the phase diagram using 99.9% and 99.5% purity ethanol, but the blends were completely insoluble for 95% purity hydrous ethanol. The high polarity of water enhances the polar part in an ethanol molecule and decreases compatibility with non-polar molecules [148]. The TGB phase diagrams for this study were constructed with the highest water content allowed by ASTM standard for gasoline–ethanol blends, and should represent the worst case scenario for TGB separation - although users should be aware that additional moisture could be introduced through the feedstock oil or be absorbed from the ambient air due to the hygroscopic nature of ethanol. National Renewable Energy Laboratory (NREL) fuel surveys have found all samples of gasoline–ethanol blends met the water specification [154]. The 1% water content used in this study should represent the worst-case scenario found in gasoline–ethanol blends at the pump, and is higher than would be expected in gasoline with low ethanol content.

To test the long-term phase physical stability of TGBs, camelina, carinata, pennycress, and canola TGBs made from 75% oil and 25% E10 were also stored for 1 year at room temperature and visually inspected. No separation was observed.

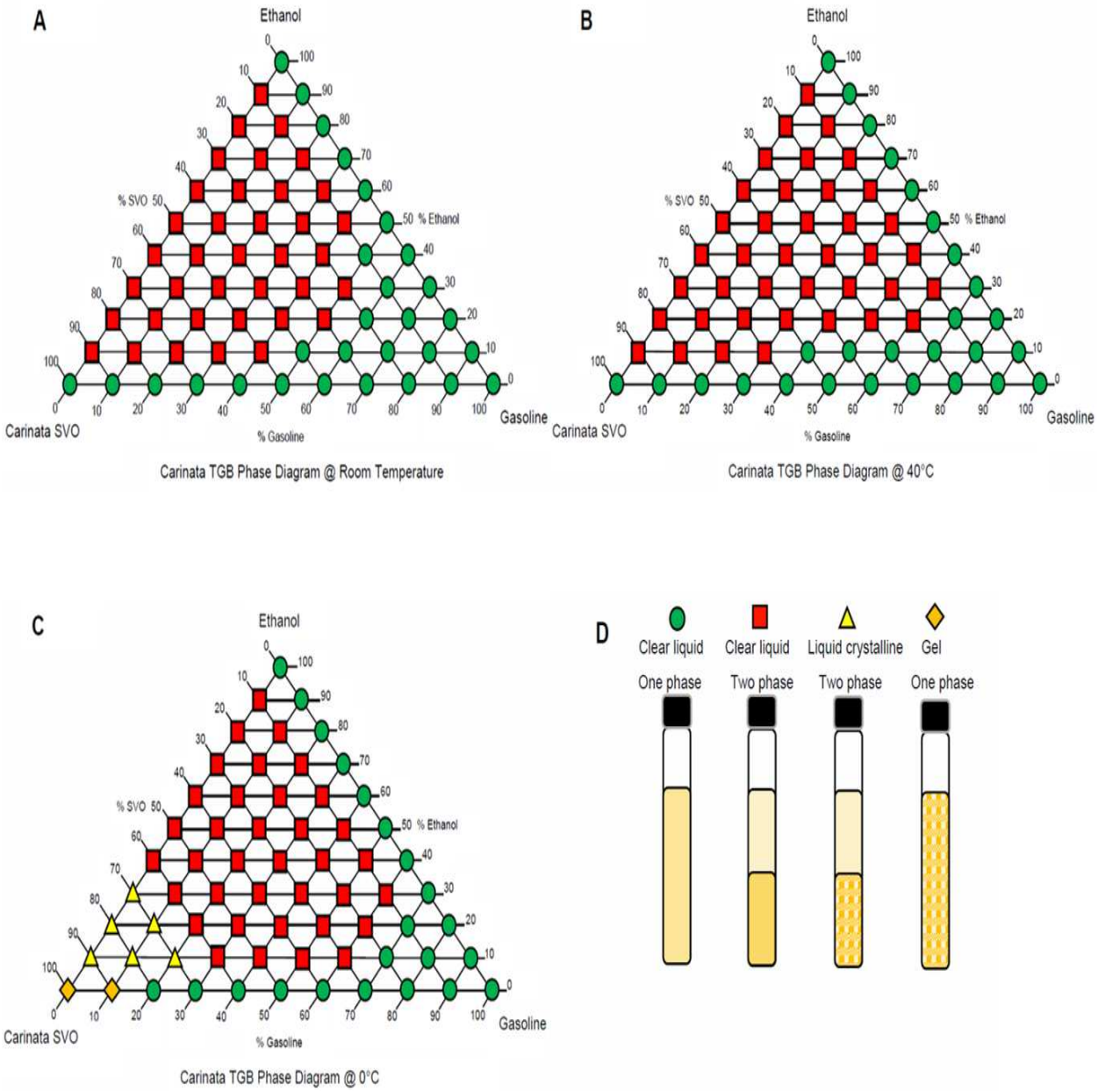

Figure 3-1. Carinata TGB phase diagrams at: room temperature (A), 40 °C (B), 0 °C (C), and legend (D).

3.3.2 Chemical stability of triglyceride blends

Figure 3-2 shows the ^{1}H NMR spectra for carinata SVO, E10, and carinata TGB overlaid. The proton resonances of the triglyceride fatty acid chains and glycerol backbone of the carinata oil in SVO correspond to what was reported in the literature [155], with olefinic protons of unsaturated fatty acids resonating at 5.3–5.5 ppm, glycerol protons resonating at 5.26, 4.1 and 4.3 ppm, methylene protons of polyunsaturated and unsaturated acyl chains at 2.78 and 2.05, protons of acyl moieties in triacylglycerols at 2.3 and 1.6 ppm, methylene envelope protons at 1.2 ppm, and methyl protons of polyunsaturated acids at 0.91 ppm and of saturated and unsaturated acids at 0.88 ppm. The proton resonances of aromatic (6.7–8.0 ppm), olefinic (4.6–6.0 ppm) and aliphatic (0.5–3.3 ppm) hydrocarbon protons in the E10 correspond to those reported for gasoline and ethanol (multiplets around 3.7 and 1.3 ppm) [152]. Comparing the different ^{1}H NMR spectra in Figure 3-2 demonstrate that TGBs are a sum of the constituent parts without any chemical changes. The TGB in Figure 3-2 was formed with a 75/25 volumetric ratio of SVO to E10. The other volumetric ratios used in testing had similar results.

This procedure was then repeated with samples from storage to ensure no chemical changes occurred over a longer timescale. First, the NMR process was repeated on the same sample three days after it was initially blended. Finally, a one year old sample was also analyzed. The time sequence testing described here all used a 75/25 blend. The results were overlaid in Figure 3-3 and confirm the chemical stability of TGBs through one year of storage. A sub-objective of the NMR time sequence testing was also to try to capture the outgassing phenomenon of TGBs. As described in Section 3.2.1, when mixing the TGBs, E10 and SVO were agitated in a HDPE container. This mixing can increase the pressure in the container due to the volatility of gasoline, and thus should be outgassed (vented) before storage. The samples in the aging and outgassing

experiments were not dissolved in deuterated chloroform as a locking solvent to ensure no interference on results and the results were manually referenced relative to the ethanol signal (multiplet at 3.6 ppm) for comparison. Evidence of venting was obtained from a relative decrease after 1 year in the ethanol peak integral at 3.6 ppm, normalized against one of the glycerol proton peak areas at 5.1 ppm, due to volatility of the ethanol. The aliphatic proton peaks near 0.88 ppm also show a reduction in normalized peak integral between day 0 and day 2, which was likely due to the more volatile short chain hydrocarbons of the gasoline venting to atmosphere during the aging and venting process.

The carinata B100 and R100 samples were also analyzed and compared to SVO. The biodiesel results are shown in Figure 3-4, and show the chemistry changes through transesterification to break the glycerine section from the fatty acid section and produce fatty acid methyl esters with a methoxy proton singlet at 3.65 ppm. These NMR results for carinata B100 were similar to other NMR research where caster and soy-based biodiesel were studied [156]. The change in chemistry for the R100 fuel from SVO is also shown in Figure 3-4. The Catalytic Hydrothermolysis process used to make the R100 converts triglycerides to a mixture of unsaturated straight chain, branched, and cyclic hydrocarbons [130].

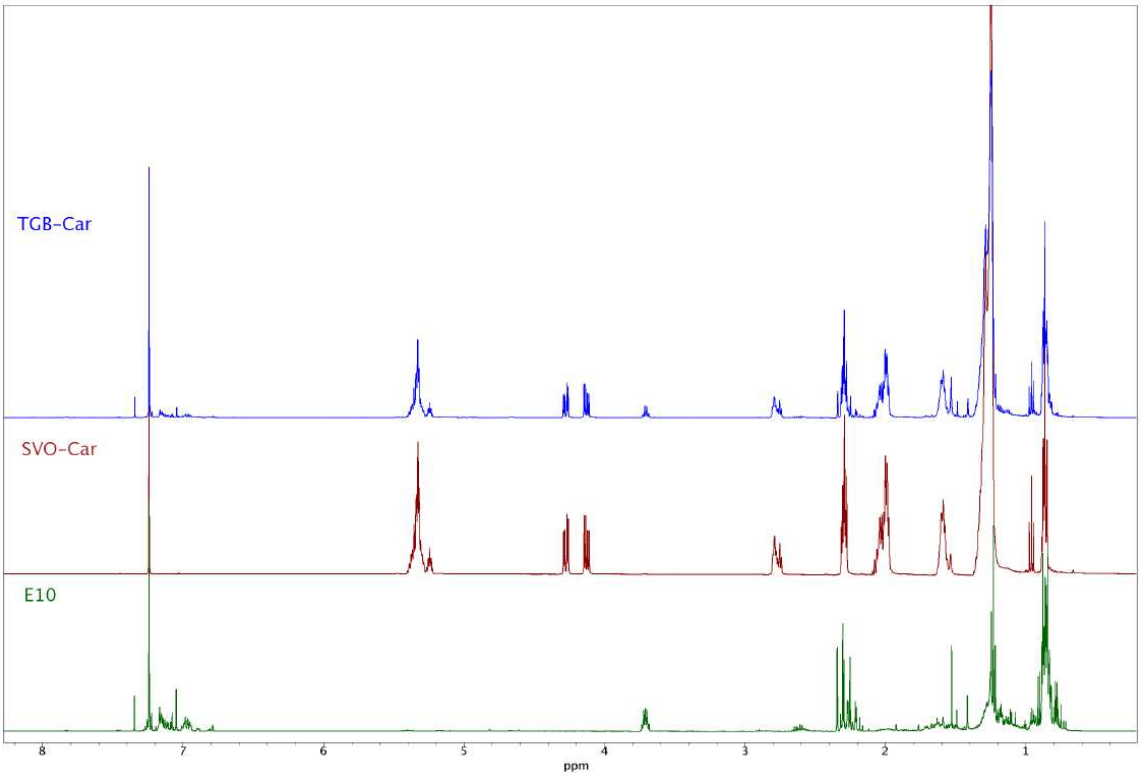

Figure 3-2. Carinata TGB and blend components NMR results.

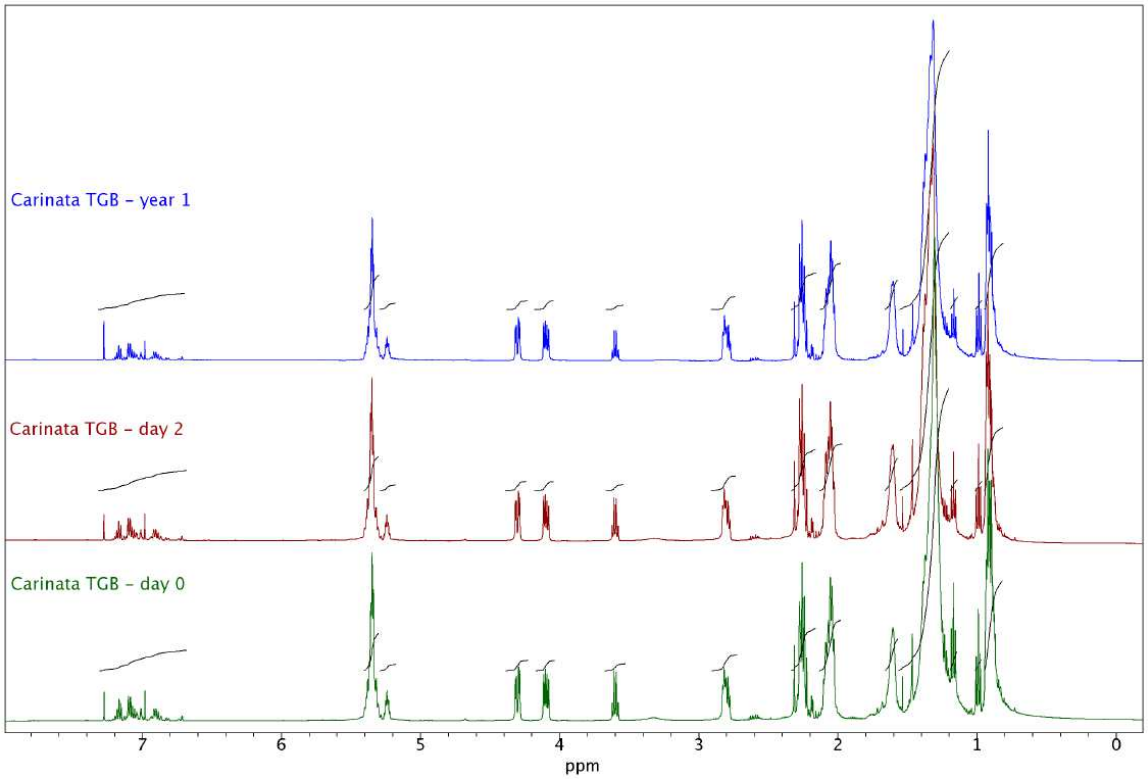

Figure 3-3. Carinata TGB time sequence NMR results.

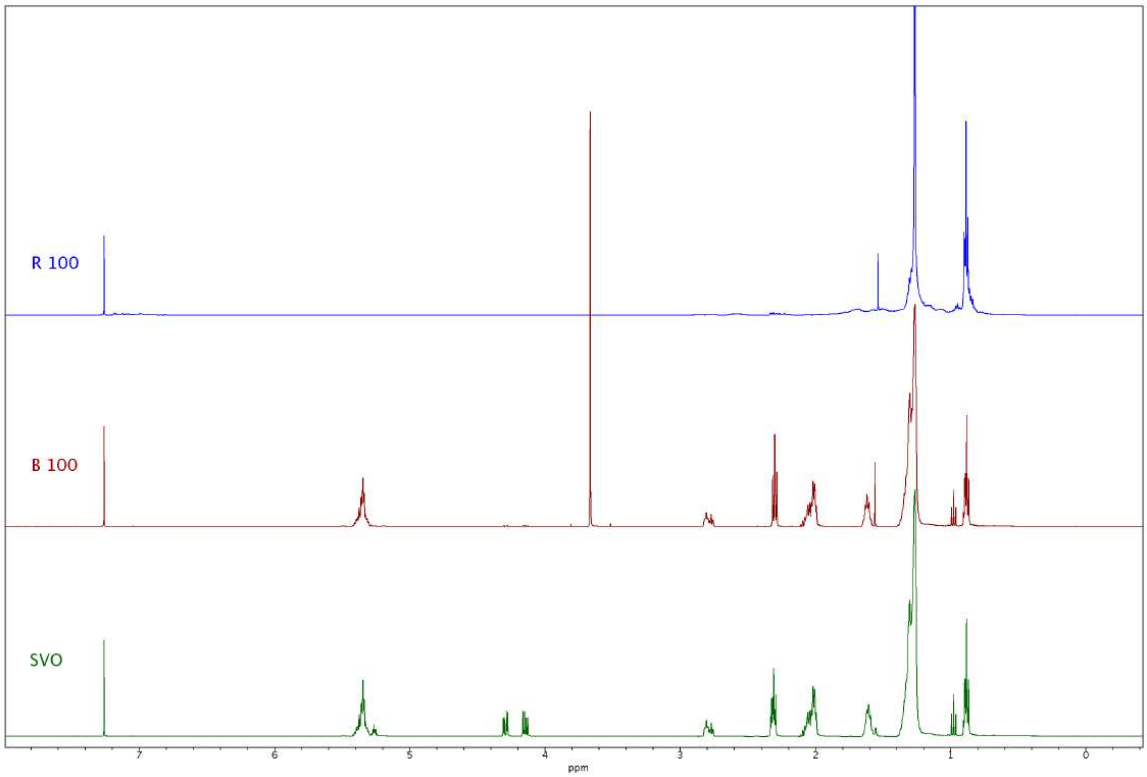

Figure 3-4. Carinata B100 and R100 NMR results.

3.3.3 Viscosity

The viscosity results for the fuels of Table 3-2 are displayed in Figure 3-5. The TGB results in Figure 3-5 were from a 75% SVO to 25% E10 blend. The acceptable range for kinematic viscosity by ASTM standard for B100 fuels @ 40 °C is 1.9–6.0 mm^2/s and for Grade No. 2-D S15 petrodiesel @ 40 °C is 1.9–4.1 mm^2/s [100], [147]. As shown by Figure 3-5, the conversion of SVO to B100 and TGB both reduced the viscosity, but there was a greater reduction through the transesterification process than by blending the oil with 25% E10. TGB viscosity results were also more variable than the B100 results; a higher viscosity SVO resulted in a higher viscosity TGB. The R100 fuels had viscosity values similar to petrodiesel. There were no significant differences between the crude and RBD results. As displayed by Figure 3-6 for the TGB sweeps, the viscosity of the blend decreased as E10 content increased. The mean value and the standard deviation for the four oil types tested are shown. The level of viscosity reduction tends to taper

off with the higher blend ratios. The use of E10 as a blending agent has a greater reduction in viscosity for each blend ratio than using petrodiesel (dilution method). A 55% canola SVO + 45% petrodiesel still had over 3X higher viscosity than the highest acceptable level for petrodiesel by ASTM standard.

The viscosity data in Figure 3-5 and Figure 3-6 was recorded at 40 °C. The viscosity of the TGBs was also recorded at a range of temperatures for carinata biofuels as shown in Figure 3-7. At some of the higher TGB blend ratios and temperatures, the gasoline volatility caused an error in the Anton Paar SVM3000 and those data points are not displayed. Figure 3-7 shows that the viscosity of petrodiesel did not vary as much as the TGBs. The change in viscosity over the temperature range was greater for the lower TGB blend ratios.

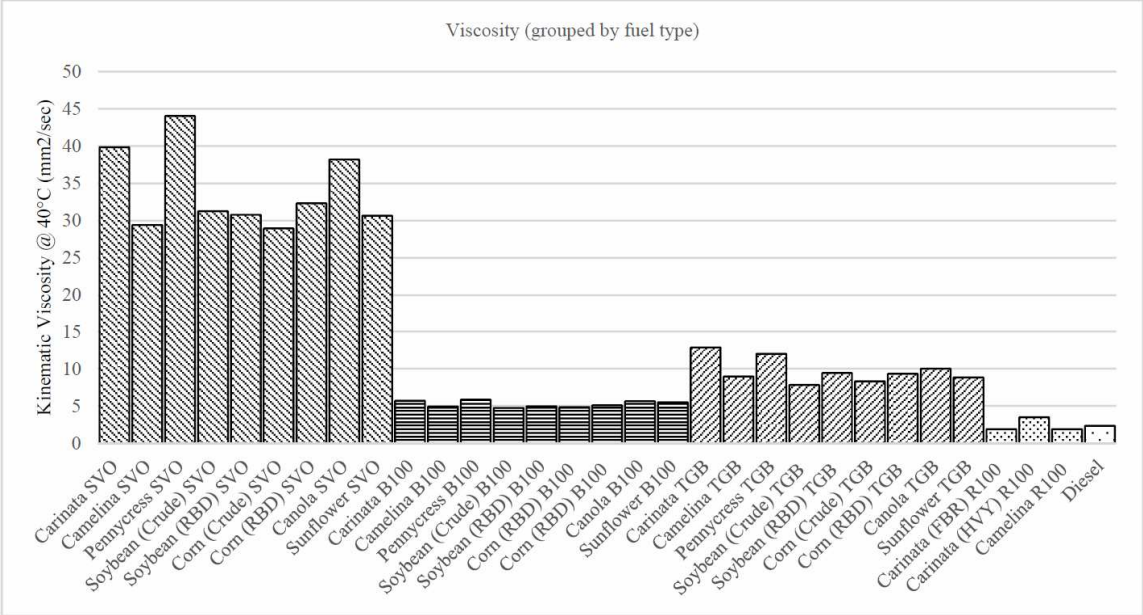

Figure 3-5. Viscosity (grouped by fuel type).

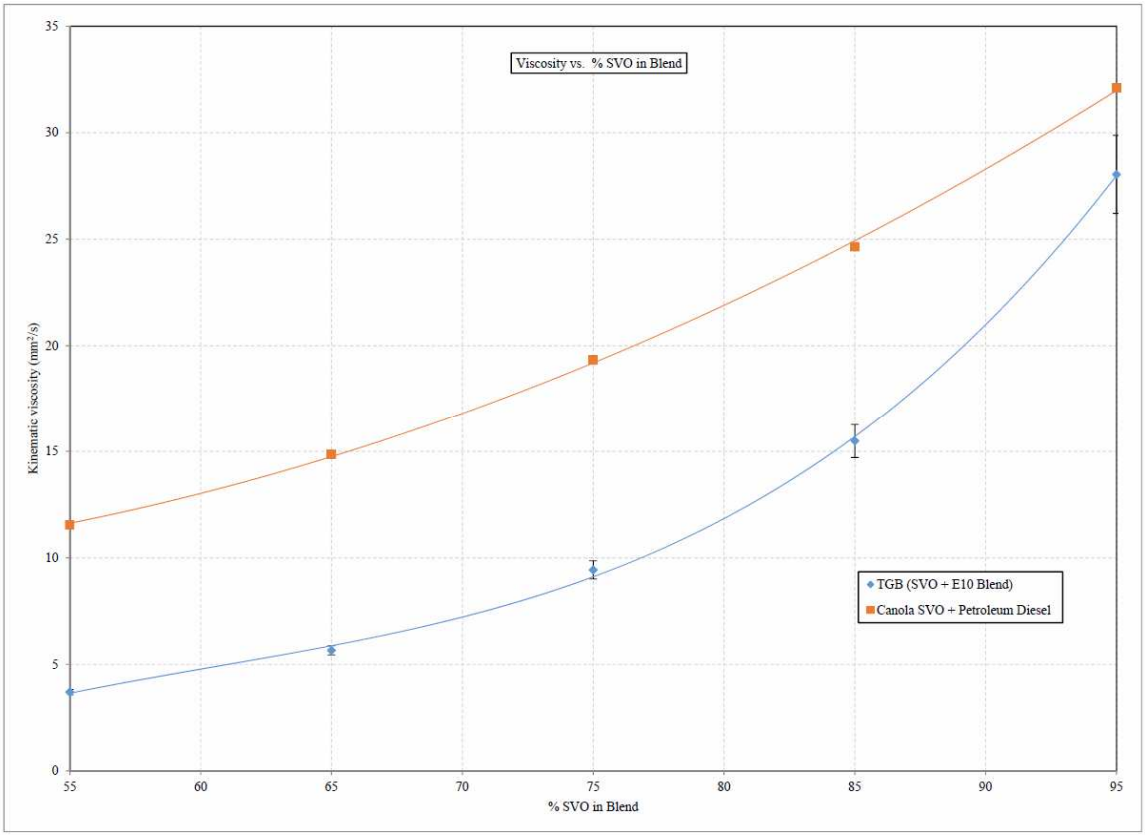

Figure 3-6. Viscosity versus percent SVO in blend.

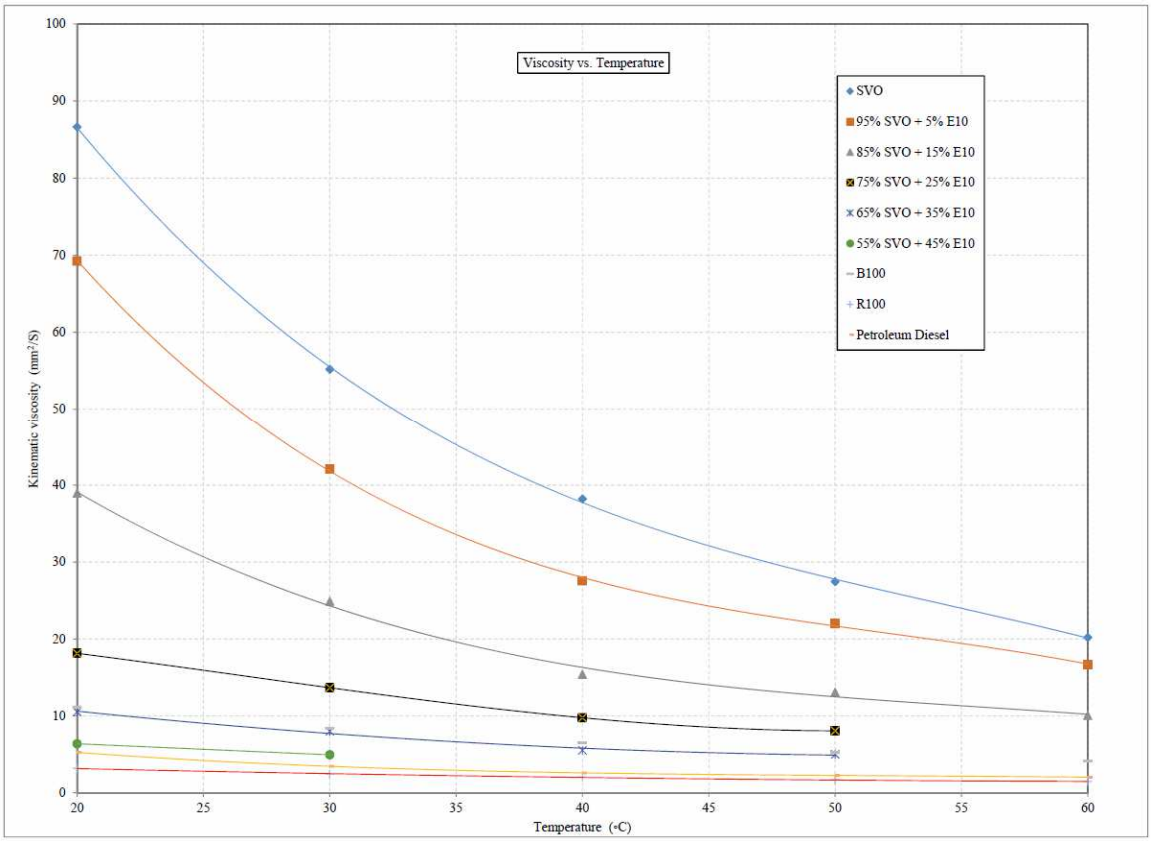

Figure 3-7. Viscosity versus temperature for carinata test fuels.

3.3.4 Density

The density results for the fuels of Table 3-2 are displayed in Figure 3-8. The biodiesels and TGBs both had reduced density compared to the SVO feedstock. There is no ASTM specification for density of biodiesel; B100 fuels that meet the other specifications in ASTM D6751 fall between 0.86 and 0.90 g/cm3 [100], as was true for all biodiesels in this study. European Biodiesel Standard EN 14214 for Vehicle Use does specify densities between 860 and 900 kg/m3 [157].

TGBs with 25% E10 used as a blending agent had density values similar, but slightly lower than biodiesel from the same feedstock. In practice, farmers using TGB biofuels either blend the fuel volumetrically, as was done in this study, or gravimetrically. For the gravimetric process, gasoline is added to SVO until the resulting TGB has a specific gravity (SG) near 0.865 [97].

The farmer uses a hydrometer as a quick and inexpensive way to measure SG and uses density to control E10 content when mixing TGBs in large quantity. Farmers using the hydrometer method have had favorable results with using TGBs as an on-farm fuel, but those new to using TGBs should be aware the SVO produced on their farm might have different fuel properties, and monitor the gasoline percentage they add to SVO with this in mind. SVO physical properties can vary by location and with agricultural practices [158]. The TGB blend sweeps in Figure 3-9 showed that density decreases approximately linearly with increasing E10 content. TGB density is similar to B100 fuels near a 75/25 ratio and near petrodiesel at a 55/45 ratio.

During engine testing, due to the lower energy content of the B100 and TGB fuels, more fuel flow was required to the engine as compared to petroleum for the same power setting. However, due to the higher density of the B100 and TGB fuels, the difference in brake specific fuel consumption (bsfc) between those biofuels and petroleum was smaller on a volumetric flow basis than on a mass flow basis. As shown in Figure 3-8, the renewable diesels in this evaluation had lower densities than petrodiesel. In the case of the R100 fuels, the engine testing performance was similar to petrodiesel on a mass flow basis, which could have performance advantages over other types of biofuels in some military applications where weight is a concern.

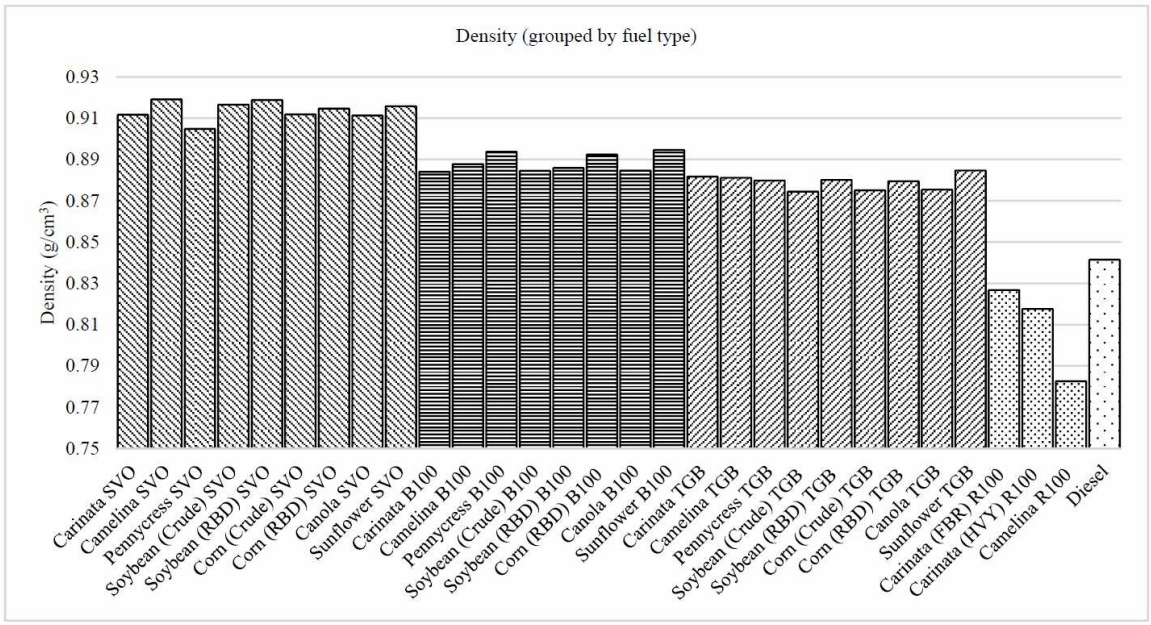

Figure 3-8. Density (grouped by fuel type).

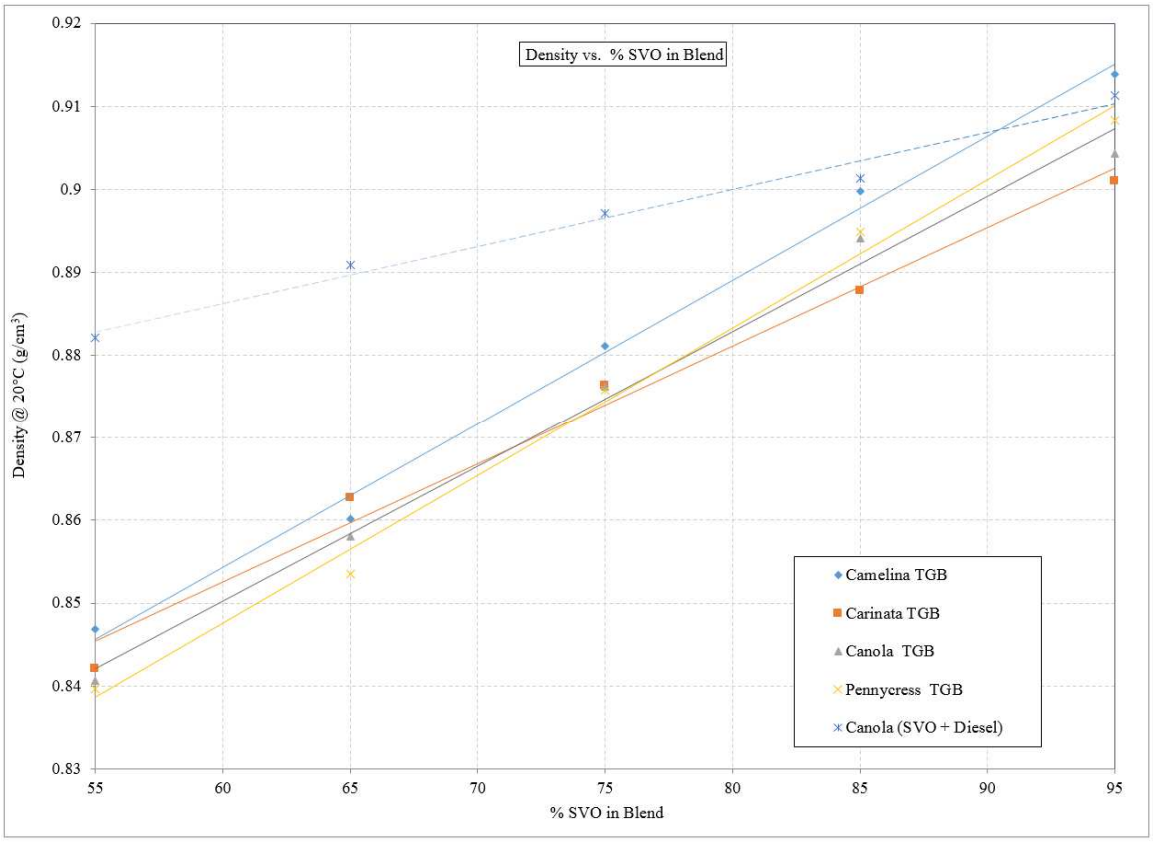

Figure 3-9. Density versus percent SVO in blend.

3.3.5 Speed of sound

The speed of sound results for the fuels of Table 3-2 are displayed in Figure 3-10. The biodiesels and TGBs both had a reduction in speed of sound as compared to the SVO feedstock. The 75/25 TGBs had speed of sound values closer to petrodiesel than biodiesels of the same feedstock, but also had more variability in the results. Differences in speed of sound of biofuels as compared to petroleum have been linked to changes in fuel injection timing [136]. The blend sweep of TGBs showed speed of sound decreased nearly linearly with increased gasoline, with a greater reduction for TGBs than the dilution method (similar to density results).

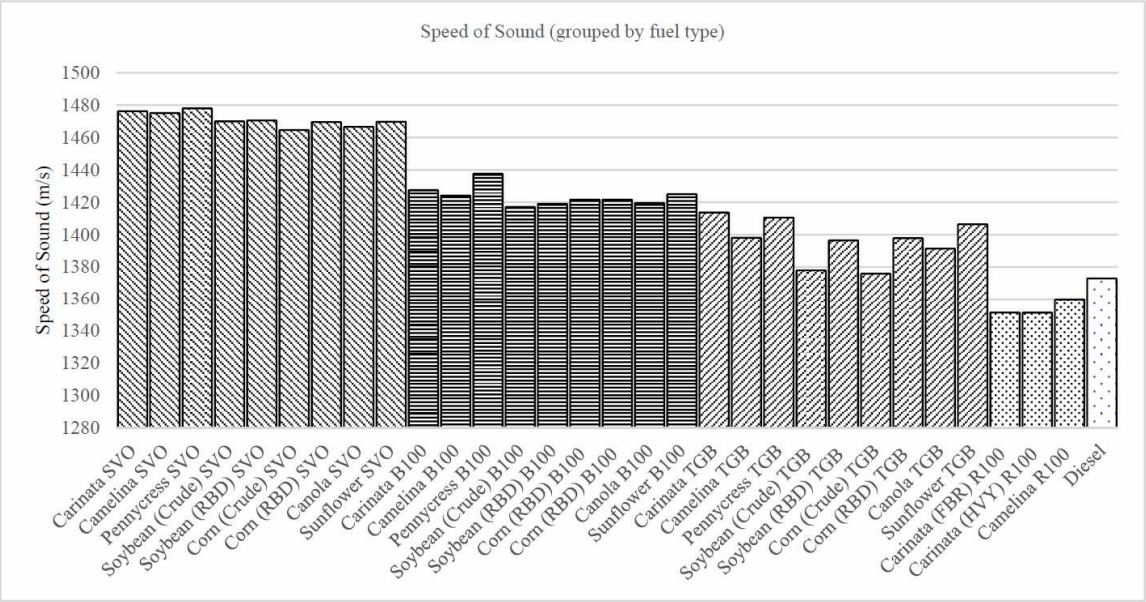

Figure 3-10. Speed of Sound (grouped by fuel type).

3.3.6 Flash point

The flash point is the lowest temperature at atmospheric pressure at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions. The B100 specification for flash point is 93 °C min while the Grade No. 2-D S15 petrodiesel specification for flashpoint is 52 °C min [100], [147]. Flash point results are shown in Figure 3-11. All B100 fuels in this evaluation met the ASTM specification and R100 fuels had similar flash points to

petrodiesel. Gasoline, by definition, is a mixture of relatively volatile hydrocarbons, so users of TGBs should use additional caution to prevent accidental electrostatic discharge ignition during their production, storage, and distribution [159]. The volatility of the gasoline caused all TGBs to have flashpoints less than 40 °C in neat form due to the low flashpoint of the gasoline (-40 °C) and ethanol (13 °C) components [160]. Even a small amount of E10 in a TGB will drive the flashpoint to a low value. When testing the blend sweeps, the 95/5 TGBs had flashpoints above 40 °C only after blended with petrodiesel as shown in Figure 3-12. Low flashpoints have also been recorded for other blends and emulsions containing ethanol currently under study, and are relatively independent of the amount of ethanol in the blend [148], [153]. The low flashpoint of these blends is typically dominated by the fuel component in the blend with the lowest flash point [148], [160], [161], [162], [163], [164]. The vapor above the fuel level in a gasoline storage container at normal ambient temperature exceeds the upper flammability limit while the vapor above the fuel level of ethanol in storage can be within the flammability limit [161], which would be another reason to limit ethanol content in the gasoline used to manufacture TGBs, in addition to the solubility concerns outlined previously. Due to flammability concerns, like other blends of this nature, TGB handling, storage, and transportation must be afforded the same cautions as neat gasoline.

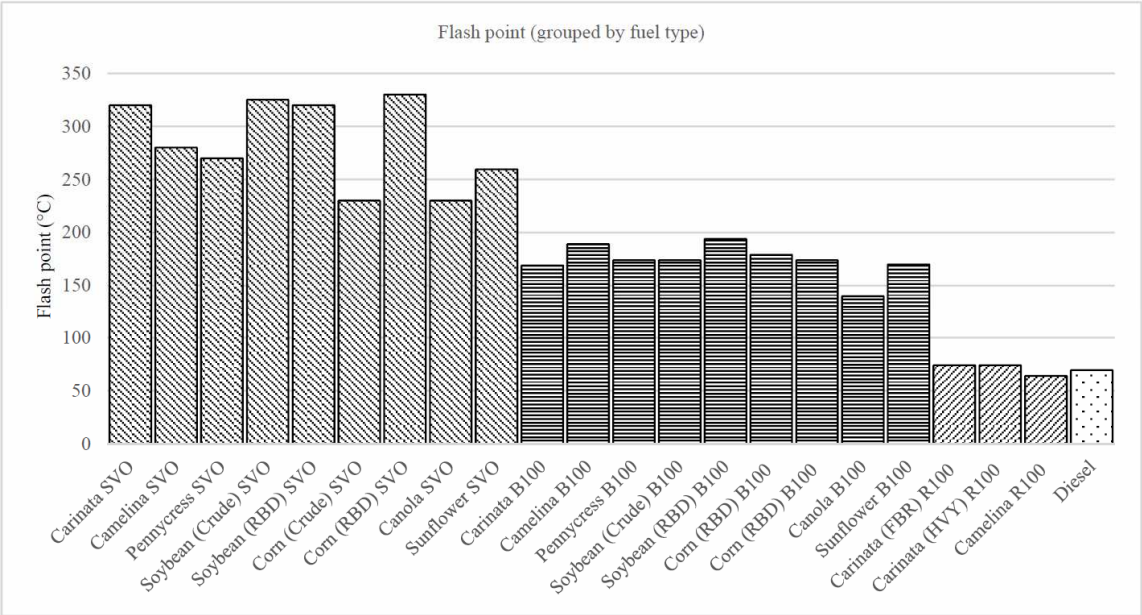

Figure 3-11. Flash point (grouped by fuel type).

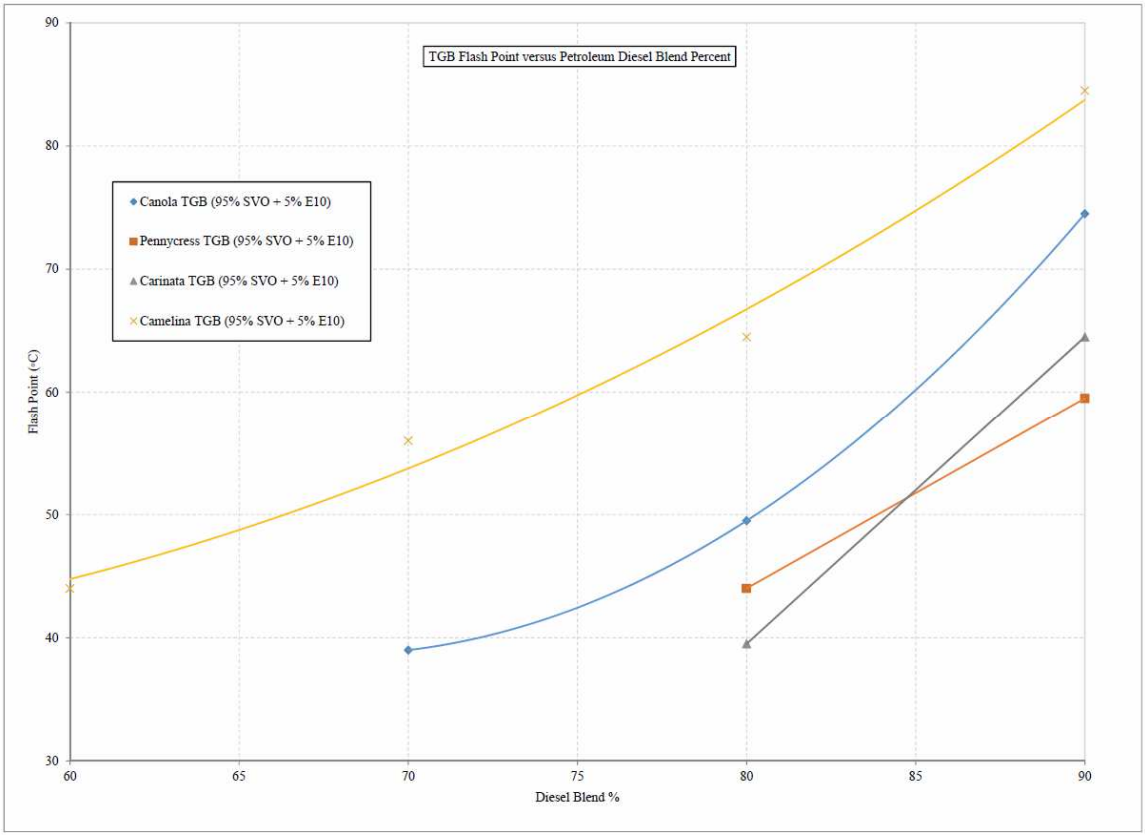

Figure 3-12. Flash point TGB + petrodiesel sweep.

3.3.7 Heating value

It is important that biofuels have energy content near the petroleum fuel it displaces. A reduced energy content of the fuel will translate into a reduction in fuel economy and in key performance parameters such as maximum horsepower and torque. The biodiesels had higher energy content than the SVO of the same feedstock as shown in Figure 3-13. The blending of SVO with higher energy gasoline (46,599 J/g) at a 75/25 ratio resulted in an overall TGB biofuel with energy content higher than biodiesel. This higher energy content contributed to lower brake specific fuel consumption (bsfc) of TGBs over biodiesels during the engine performance testing [137]. The renewable diesel fuels had energy content higher than the other biofuels and similar to petrodiesel. TGB blend sweep testing showed that energy content increased approximately linearly as gasoline content was increased.

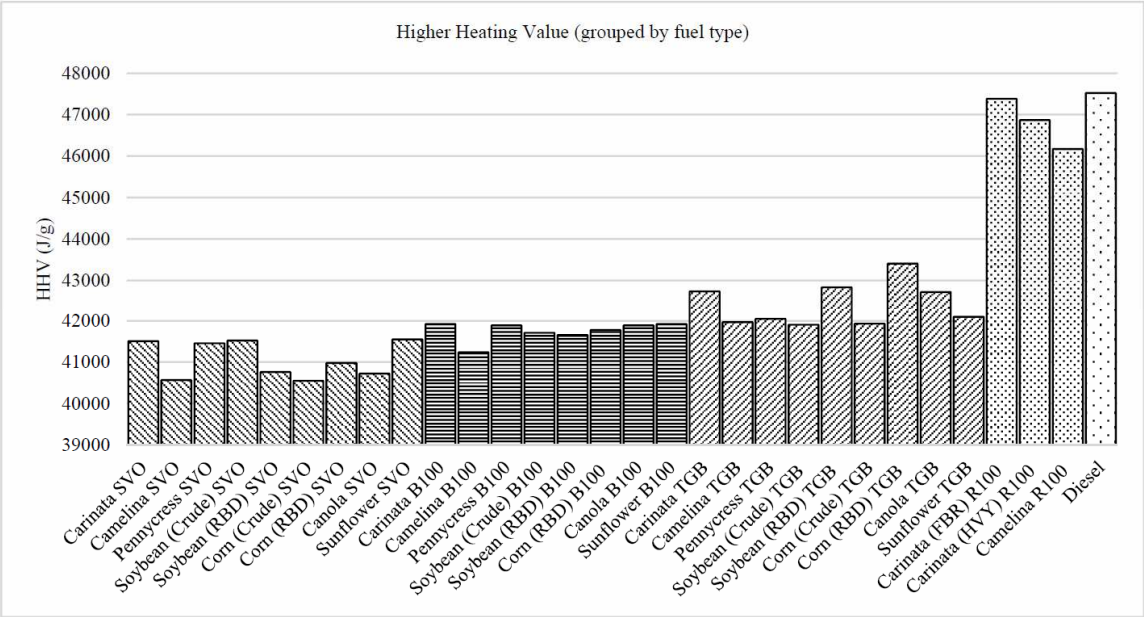

Figure 3-13. Calorific value (grouped by fuel type).

3.3.8 Cold flow properties

Cold flow properties are extremely important for any fuel used in cold climates. When SVO is converted to B100 or TGB, one of the purposes is to improve the cold flow properties. The

SVOs in this study all had CFPP values at or near room temperature. For all feedstocks, the conversion to biodiesel improved the CFPP by approximately 25 °C. One positive outlier was biodiesel produced from pennycress oil which had a CFPP result of -18 °C, (-17 °C [45]). This is good news for widespread adaption in the Midwestern U.S. where the crop is being developed as an off-season crop in a traditional corn and soybean rotation. Farmers using pennycress biodiesel could continue to use this biofuel through much of the year. Pennycress TGBs had a CFPP more similar to the other feedstocks. The renewable diesels performed similar to the petroleum fuel they intend to displace. The results are shown graphically in Figure 3-14.

The cold flow properties of the 75/25 TGBs were much improved over SVO, and slightly better than biodiesel for most feedstocks. A blend sweep of TGBs, displayed in Figure 3-15, shows a small amount of gasoline greatly improved the cold flow properties. The benefit to plug point tapers off with gasoline content higher than 25%. Figure 3-15 also shows the CFPP for the dilution method. Gasoline was much more effective as a blending agent than petrodiesel for reducing CFPP.

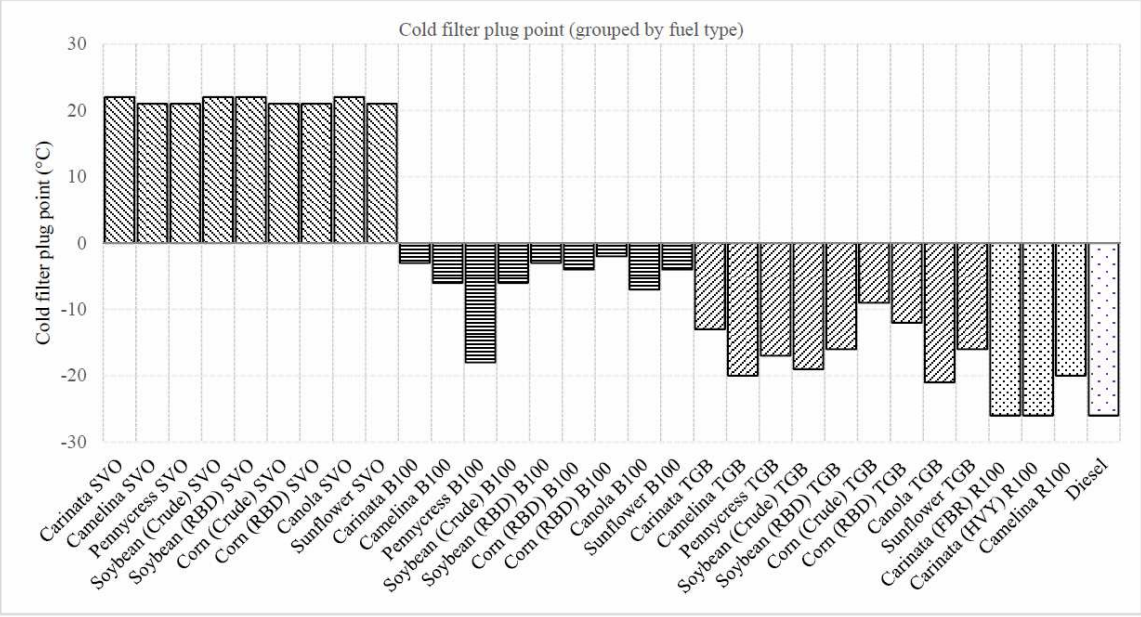

Figure 3-14. Cold filter plug point (grouped by fuel type).

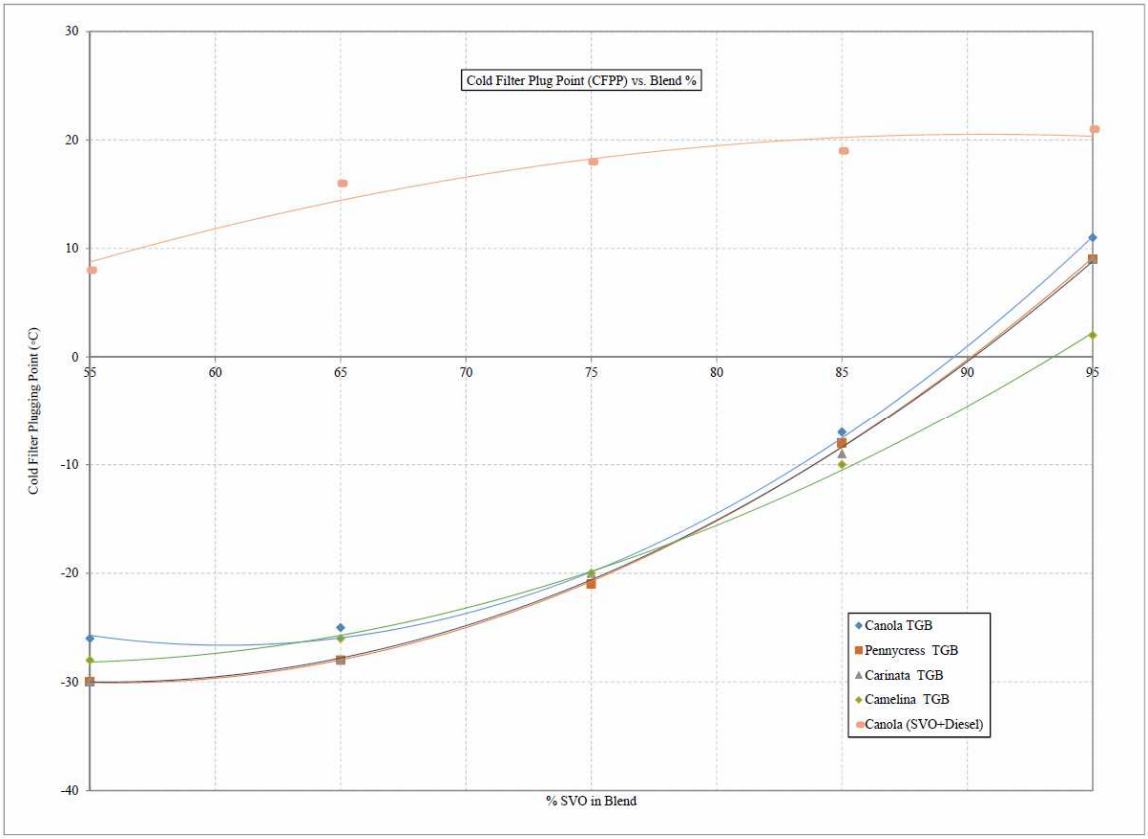

Figure 3-15. Cold filter plug point versus percent SVO in blend.

3.3.9 Lubricity

Lubricity of fuel is important for the proper long-term functionality of engine components such as fuel pumps and injectors [165]. Biodiesel and SVO have shown inherent lubricity in both neat form and when used as an additive to petrodiesel [166].When the U.S. Environmental Protection Agency phased in use of Ultra Low Sulfur Diesel (ULSD), removal of the sulfur-containing components caused the lubricity of the conventional petrodiesel fuel to be significantly reduced or even eliminated. Adding biodiesel or SVO to ULSD conventional petrodiesel fuel has been shown to restore the lubricity, even in small amounts (1–2%) [167]. Use of SVO and biodiesel as lubricity additives has an advantage over some lubricity additives due to their inherent fuel value.

Lubricity of SVO and biodiesel has been tested for several conventional feedstocks and blends. In previous testing, biodiesel was slightly more effective than SVO for equal treatment rates [168]. Past research also showed biofuels made from crude oil also had better lubricity than biofuels made from RBD oil [169]. The results of the lubricity evaluation of a TGB formed from a 75% crude soybean oil + 25% E10 is shown in Table 3-4 along with petrodiesel standards and previously published lubricity data for other soy-based biofuels. Note that the historical results cited here for the petrodiesel + biofuel blends depend strongly on the lubricity of the base petrodiesel.

The TGB lubricity result of 108 μm show TGB maintains the inherent lubricity found in other types of biofuels. Additional testing using TGB blend sweeps would reveal how lubricity changes with gasoline and ethanol content in the TGB. Previous research using fuel blends containing ethanol (ethanol + biodiesel + petrodiesel) showed that increasing ethanol content in the blend did not result in significant loss of lubricity until the ethanol content was near 100% [170].

Table 3-4. Lubricity test results.

FUEL TYPE	FEEDSTOCK		AVERAGE WEAR SCAR DIAMETER (WSD) @ 60 °C (μm)	REFERENCE
	TYPE	REFINEMENT		
Diesel standard for maximum wear scar	Petroleum		520	ASTM D975 [147]
TGB	Soybean	Crude	108	
98% $Diesel_1$ + 2% B100 Blend			375	Hu et al. [169]
B100			155	Hughes et al. [171]
99% $Diesel_2$ + 1% SVO Blend		RBD	319	Van Gerpen et al. [168]
99% $Diesel_2$ + 1% B100 Blend			251	Van Gerpen et al. [168]
98% $Diesel_1$ + 2% B100 Blend			540	Hu et al. [169]
B100			136, 159	Holser et al. [39], Moser [172]

Notes:

SVO = straight vegetable oil
B100 = 100% biodiesel
TGB = triglyceride blend (75% vegetable oil + 25% E10 gasoline (v/v)
RBD = refined, bleached, deodorized

Subscripts:

$_1$ = basof study had WSD of 720 μm
$_2$ = base diesel of study had WSD of 376 μm

3.3.10 Fatty acid profiles

The fatty acid (FA) profile of the seven oils used in this evaluation is provided for reference in Table 3-5. The chromatography was performed on an Agilent Technologies 7890A Gas

Chromatograph. One advantage of industrial oils is their FA profiles can be optimized for fuel conversion and quality instead of favorable food characteristics. The production of very long-chain fatty acids (VLCFAs), with chain length of 20 carbon (C20) or more, have a wide variety of industrial uses [53].

Table 3-5. Fatty acid profile for oils in evaluation.

Designation:	Common Name:	Formula:	Carinata	Camelina	Pennycress	Soy (Crude)	Soy (RBD)	Canola	Sunflower	Corn (Crude)	Corn (RBD)
C14:0	Myristic	$C_{14}H_{28}O_2$	0.05	0.05	0.07	0.07	0.07	0.04	0.07	0.03	0.03
C16:0	Palmitic	$C_{16}H_{32}O_2$	2.95	5.25	2.57	10.03	10.02	3.31	6.31	11.36	11.12
C16:1	Palmitoleic	$C_{16}H_{30}O_2$	0.15	0.14	0.19	0.10	0.10	0.23	0.14	0.12	0.14
C18:0	Stearic	$C_{18}H_{36}O_2$	1.09	2.32	0.38	5.44	5.45	1.98	3.18	1.76	1.84
C18:1	Oleic	$C_{18}H_{34}O_2$	10.63	18.11	11.06	26.06	26.15	76.85	30.24	28.81	31.16
C18:2	Linoleic	$C_{18}H_{32}O_2$	15.03	19.41	19.52	49.41	49.36	12.72	58.47	52.60	53.06
C18:3 Alpha	α-Linolenic	$C_{18}H_{30}O_2$	13.52	32.29	10.15	7.47	7.05	1.37	0.07	2.97	1.30
C18:3 Gamma	γ-Linolenic	$C_{18}H_{30}O_2$	0.04	0.17	0.05	0.03	0.30	0.02	0.00	0.02	0.08
C20:0	Arachidic	$C_{20}H_{40}O_2$	0.87	1.31	0.22	0.41	0.42	0.67	0.24	0.43	0.42
C20:1	Gadoleic	$C_{20}H_{38}O_2$	7.69	13.35	9.58	0.22	0.23	1.31	0.17	0.33	0.35
C20:2	Eicosadienoic	$C_{20}H_{36}O_2$	0.98	1.60	1.68	0.04	0.04	0.05	0.00	0.03	0.03
C20:3	Eicosatrienoic	$C_{20}H_{34}O_2$	0.31	1.02	0.32	0.00	0.00	0.00	0.00	0.00	0.00
C22:0	Behenic	$C_{22}H_{44}O_2$	0.74	0.30	0.14	0.36	0.36	0.34	0.66	0.13	0.14
C22:1	Erucic	$C_{22}H_{42}O_2$	39.67	2.48	36.55	0.02	0.00	0.11	0.00	0.00	0.00
C22:2	Clupanodinic	$C_{22}H_{40}O_2$	1.20	0.11	0.69	0.00	0.00	0.00	0.09	0.00	0.00
C22:3	dihomo-γ-linolenic	$C_{20}H_{34}O_2$	0.08	0.22	1.42	0.00	0.00	0.00	0.00	0.00	0.00
C23:0	Tricosylic	$C_{23}H_{46}O_2$	0.28	0.27	0.08	0.00	0.00	0.00	0.00	0.00	0.00
C22:4	Adrenic	$C_{22}H_{36}O_2$	0.17	0.05	0.08	0.00	0.00	0.00	0.00	0.00	0.00
C24:0	Lignoceric	$C_{24}H_{48}O_2$	0.55	0.24	0.08	0.12	0.12	0.15	0.26	0.17	0.17
C24:1	Tetracosenoic	$C_{24}H_{46}O_2$	2.04	0.69	3.56	0.00	0.00	0.13	0.04	0.14	0.04

3.4 Conclusions

This study focused on using industrial oils in combination with TGBs as an on-farm fuel pathway since the commercial market for these oils is still emerging. The TGB blend percentage of vegetable oil to E10 gasoline was varied to evaluate its effects on fuel properties. Many fuel properties were improved with the addition of gasoline to SVO. The exception was flash point, and users of TGBs should handle and store with the same caution as gasoline. The physical and chemical properties of TGBs were studied through phase diagrams and NMR spectroscopy. Users of TGBs should limit the ethanol content in the gasoline to E10 to ensure solubility. Chemical stability of TGBs was demonstrated for up to one year of storage. There were no significant differences in the fuel properties measured for the crude and refined fuels. Overall,

this fuel property evaluation and recent engine testing has shown the use of TGBs may fill a niche as a sustainable fuel pathway for farmers wanting to introduce these new crops into their rotation and use the oil for on-farm fuel needs. TGBs may also be well suited for local use of vegetable oils as fuel in remote areas. Future research will include long-term durability of TGBs in compression ignition engines.

Chapter 4. EVALUATION OF INDUSTRIAL CORN OIL AS AN ON-FARM BIOFUEL FEEDSTOCK[3]

4.1 Introduction

Farm use of petrodiesel fuel is significant, especially in the Midwestern U.S. region where consumption tops 1.5 billion gallons annually [173]. In Iowa, Nebraska, and South Dakota, farm use of distillate fuel oil is more than 20% of total consumption [173]. Fuel and other energy-inputs (fertilizer, lube, and electricity) represent 60% of total operating expenses for some crop farmers [174]. The USDA found that increases in energy-related production costs generally lower agricultural output, raise prices of agricultural products, and reduce farm income [174]. One way to combat increased fuel input costs would be for farmers to produce their own biofuels. Like the transportation sector and military users, the agricultural use of locally sourced renewable fuels could help lower costs, improve energy security, bolster rural economics, and have positive environmental impacts.

This research explores the feasibility of using corn oil as an on-farm biofuel feedstock. The yellow dent corn kernel contains a small amount of oil (~3.8%) which can be extracted during the production of ethanol. Only the starch portion of a corn kernel is converted to ethanol; the remaining solids (including the oil) remain in the distillers grain co-product. The ethanol industry has recently discovered economical methods to extract this corn oil from the meal stream. Industry experts estimate 85% of U.S. dry mill ethanol facilities are now using some form of corn oil extraction, producing 300 million gallons of corn oil annually [175], [176]. Since most ethanol plants are non-food grade (NFG) facilities, distillers corn oil from an ethanol plant is an industrial oil (not generally regarded as safe (GRAS) for human consumption). Industrial corn oil

[3] Manuscript accepted for publication, *Applied Engineering in Agriculture* by A.C. Drenth et al. [202]

(ICO) represents a relatively new, abundant, and economical source of biofuel feedstock. The current price for this crude corn oil is $0.27 per pound, or about $2.06 per gallon (February 2015 average FOB spot bids reported by ethanol plants) [177]. The use of ICO for local on-farm fuel would be mutually beneficial to the farmer and the ethanol plant as an additional market for the oil, with potential savings in storage, transportation, and retail margins for both parties. ICO from a local ethanol plant has several benefits over most conventional oilseed options like soybean, canola, and sunflower for farmers looking to produce their own fuel. No crushing/oil extraction hardware is necessary, saving significant costs and time investment. Another benefit is that fresh oil is available on a year round basis. Finally, the economics of on-farm fuel from conventional oilseeds often depend on using the coproduct meal at an animal feedlot [112]; the use of ICO would not depend on the value/need for meal and would open the door for grain farmers who do not own livestock. Many farmers and ethanol plants already have symbiotic relationships through the sale and delivery of corn, stover, and meal.

The main objective of this research was to conduct compression ignition (CI) engine performance and fuel property evaluations of ICO based biofuels as compared to petrodiesel. The fuel pathways used were triglyceride blend (TGB), biodiesel (B100), and renewable diesel (R100). A TGB is a mixture of vegetable oil and another less viscous fuel (other than petrodiesel). Previous engine research using E10 gasoline as a blending agent at a 75% vegetable oil to 25% E10 volumetric ratio found this TGB compatible with CI engines without modification [137]. This research was focused on TGBs made from ICO due to the ease of creating this biofuel for farmers, and represents the first published engine performance data and fuel property data for multiple TGB blend types and ratios. Biodiesel is fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [100]. The B100

fuel pathway is also feasible at a farm-scale and biodiesel-petrodiesel blends are now covered under warranty by many engine manufactures. Additionally, there may be tax advantages or other incentives for farmers choosing this option [93]. Renewable diesel is a non-ester renewable fuel that is pure hydrocarbons and indistinguishable from petrodiesel but made from biomass [130]. R100 is not feasible to produce at a farm-scale but was included here for comparison and due to interest in this pathway by the military and transportation sector.

4.2 Experimental setup

4.2.1 Test fuel preparation

All biofuels in this evaluation used ICO as feedstock. The TGBs were formed by first filtering ICO with a 10 μm polypropylene filter. The filtered oil was then mixed with the blending agent (gasoline with various ethanol contents or renewable naphtha) at three volumetric ratios. The resulting TGB was agitated in a high-density polyethylene (HDPE) container to ensure adequate mixing before filtering again to 1 μm. ICO was also converted to biodiesel via transesterification (alcoholysis) by Renewable Energy Group (REG-9000™ Biodiesel). Biodiesel is produced by a reaction of the esters in vegetable oil (or animal fat) with an alcohol in the presence of a catalyst to yield mono-alkyl esters of long chain fatty acids and glycerol, which is removed [100]. Renewable diesels are non-ester, petrodiesel-like fuels derived from biological sources which can be produced using various methods [79]. Applied Research Associates (ARA) provided the renewable diesel (ReadiDiesel®) for the evaluation. Renewable, Aromatic, Drop-in Diesel (ReadiDiesel®) is produced using the Biofuels ISOCONVERSION (BIC) process, which combines ARA's Catalytic Hydrothermolysis (CH) process and Chevron Lummus Global's (CLG) hydroprocessing technology. The BIC process allows the production of renewable diesel, jet, and naphtha fractions from the same batch. ARA also provided the renewable naphtha used

in the evaluation, also created with ICO via BIC. The approximate properties of the renewable naphtha are 1.5 mass % benzene, 60-65 mass % n-paraffins and ~30 mass % cycloparaffins.

4.2.2 Engine performance test setup

Engine performance and emission assessments of the test fuels were conducted using a 4.5 liter, 175 hp, John Deere (Moline, Illinois) 4045 PowerTech Plus test engine that meets Tier 3/Stage IIIA emissions specifications. A Dynesystems (Jackson, Wisconsin) Midwest 1014A eddy current dynamometer and Dynesystems Dyn-LocIV dynamometer controller was used to maintain a constant engine speed. The standard fuel tank is filled with petrodiesel and a three way solenoid valve and lift pump is used to deliver test fuels from an auxiliary fuel tank. Fuel flow is measured by a Micro Motion (Boulder, Colorado) 2700R11BBCEZZZ corriolis meter. A Kistler (Novi, Michigan) piezoelectric pressure transducer (type 6056A41: -20 pC/bar sensitivity) installed in the glow plug port of cylinder 1 using adaptor (6542Q128) was used to record in-cylinder pressure data. A National Instruments (Austin, Texas) PXI-1002 connected to a Kistler charge amplifier (type 5010) were used to record high speed combustion data from the in-cylinder pressure. Known geometry of the cylinder and connecting rod were used to calculate the cylinder volume as a function of crank angle. In-cylinder high speed pressure data versus volume curves were then used to calculate the apparent rate of heat release due to fuel combustion in the cylinder. A low pass Inverse Chebyshev filter with an order number of 7 and the low cutoff frequency of 0.25 was used to filter the oscillations due to the time derivative of pressure in the heat release curves. Pressure and temperature data for several engine locations were logged via National Instruments data acquisition software (DAQ) virtual instrument (VI) in LabVIEW. Engine control unit (ECU) data was also recorded.

The test engine exhaust stream is sampled by two different probes. One probe extracts exhaust for gaseous emissions measurements. Criteria pollutant measurements were made using a Rosemount (Chanhassen, Minnesota) 5-gas emissions analysis system (oxides of nitrogen (NO_x), total hydrocarbons (THC), oxygen (O2), carbon monoxide (CO) and carbon dioxide (CO_2)). A Thermo Fisher Scientific (Waltham, Massachusetts) Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer was used to obtain speciated measurement of a wide range of species including hydrocarbons through C4 and a variety of hazardous air pollutants and volatile organic compounds (VOCs). The second exhaust probe samples a small portion of the exhaust stream for particulate matter (PM). All of the PM measurements were taken after the exhaust sample is diluted with clean air in a mini dilution tunnel. PM is collected from the dilution tunnel on Whatman PLC (Piscataway, New Jersey) 7592-104 46.2 mm filters which are weighed before and after the test using a Mettler-Toledo (Columbus, Ohio) MX5 microbalance with a precision of 1 μg. Additional details about the hardware used in engine testing are available in other publications [97], [131], [137].

4.2.3 Engine performance testing procedure

Engine performance and emissions data was recorded at 50% load and intermediate speed (250 N-m and 1700 rpm), which corresponds to mode 7 of ISO 8178 Non-Road Steady Cycle (NRSC). After switching to test fuel, fuel flow was adjusted by the ECU to hold desired load, and the engine was allowed to stabilize. Once steady state was achieved, data was collected for 10-minute intervals. Between each biofuel run, the engine was operated on petrodiesel to purge the system of test fuel. Petrodiesel data was also recorded at intermediate points in the evaluation. The engine performance test runs are shown in Table 4-1 and sources of testing materials shown in Table 4-2.

Table 4-1. Engine performance and emissions test runs.

RUN #	FUEL TYPE	BLEND TYPE
1	DIESEL	*N/A*
2	TGB	85% Corn Oil + 15% E10
3	TGB	85% Corn Oil + 15% E85
4	TGB	85% Corn Oil + 15% NAP
5	DIESEL	*N/A*
6	TGB	75% Corn Oil + 25% E0
7	TGB	75% Corn Oil + 25% E10
8	TGB	75% Corn Oil + 25% E30
9	TGB	75% Corn Oil + 25% E50
10	TGB	75% Corn Oil + 25% E85
11	TGB	75% Corn Oil + 25% NAP
12	DIESEL	*N/A*
13	TGB	65% Corn Oil + 35% E10
14	TGB	65% Corn Oil + 35% E85
15	TGB	65% Corn Oil + 35% NAP
16	DIESEL	*N/A*
17	B100	*N/A*
18	R100	*N/A*

Notes:

B100 = 100% biodiesel	TGB = triglyceride blend
R100 = 100% renewable diesel	NAP = renewable naphtha

Table 4-2. Source of testing materials.

MATERIAL	SOURCE	LOCATION
Industrial Corn Oil (ICO)	Nebraska Corn Processing, LLC	Cambridge, Nebraska, USA
Renewable Diesel (R100)	Applied Research Associates, Inc.	Panama City, Florida, USA
Biodiesel (B100)	Renewable Energy Group Albert Lea, LLC	Albert Lea, Minnesota, USA
E0 Gasoline	Hill Sinclair	Greeley, Colorado, USA
E10, E30, E50, E85 Gasoline	Agfinity Cooperative	Eaton, Colorado, USA
Anhydrous Ethanol, ACS/USP Grade	Pharmco-Aaper	Brookfield, Connecticut, USA
Renewable Naphtha (NAP)	Applied Research Associates, Inc.	Panama City, Florida, USA
Diesel Fuel, Grade No. 2-D S15	Team Petroleum, LLC	Fort Collins, Colorado, USA

4.2.4 Fuel analysis procedure

Biofuels should have similar fuel properties as the petroleum fuels they intend to replace and must also be physically and chemically stable during the normal timescale of use. TGB physical stability (solubility of the blend components) was tested using phase diagrams. TGBs formed from ICO + E0 gasoline + anhydrous ethanol, ICO + E0 gasoline + 99% purity ethanol (1% water by mass), and ICO + naphtha were tested. The volumetric content of each component was varied in 10% increments using an Eppendorf (Hamburg, Germany) Reference pipette. The resulting blend was stored in Kimble Chase (Vineland, New Jersey) screw thread glass culture tubes and shaken until thoroughly mixed. The tubes were left motionless for 10 days at room

temperature and then visually inspected for separation. The process was repeated at reduced (0°C) and elevated temperature (40 °C).

^{1}H nuclear magnetic resonance (NMR) spectroscopy was used to determine if there were any chemical changes or degradation in the components. To test the chemical stability, TGBs were formed from ICO + E10 gasoline at five volumetric ICO to E10 ratios (v/v): 95/5, 85/15, 75/25, 65/35, and 55/45. Approximately 24 hours after the blends were mixed, 75 µL of the blends were dissolved in 675 µL deuterated chloroform. ^{1}H NMR spectra were collected on a 500 MHz Varian Inova (Santa Clara, California) NMR spectrometer equipped with VJ-4.x software and using a 5 mm broadband probe. The following parameters were used: 5.477 µs 90 pulse lengths, 8003 Hz spectral widths, 32 transients with 32k data points and 30 s relaxation delays. Chemical shifts were referenced in parts per million (ppm) relative to the signal of chloroform at 7.26 ppm. The corn straight vegetable oil (SVO) and E10 were also analyzed by themselves to determine a baseline of each blend component. Finally, corn based B100 and R100 samples were also used in the analysis.

Several important fuel properties were also measured in this evaluation. Of particular interest was the effects blend type and ratio had on important fuel properties. An Anton Paar (Graz, Austria) SVM3000 Viscometer was used to measure viscosity in accordance with ASTM test method D445. An Anton Paar DSM5000 was used to measure density in accordance with ASTM D4052. Energy content needed for engine performance calculations was determined by an IKA (Wilmington, North Carolina) C200 bomb calorimeter in accordance with ASTM D240. IKA C 723 benzoic acid calibration pellets were used to verify the calibration of the calorimeter. All calibration runs had errors less than 1%. IKA C9 gelatin capsules were used to contain the test fuel to prevent any volatility loss of fuel during the calorimeter testing prior to ignition. Finally,

Cold Filter Plugging Point (CFPP) was measured in accordance to ASTM D6371 using a Lawler (Edison, New Jersey) DR4-14 Automatic Cold Flow Property Tester.

4.3 Test results

4.3.1 Brake specific fuel consumption and thermal efficiency results

Brake specific fuel consumption (BSFC) is a frequently used metric to describe engine efficiency. A low value for BSFC is desirable since at a given power level less fuel will be consumed. Figure 4-1 shows the BSFC for all fuels used in the evaluation. Data was collected at 2 hertz over the 10-minute run; the following graphs show the mean value of the run(s) with one standard deviation from the mean showing uncertainty and indicated by error bars. The results show the engine fuel consumption was fairly insensitive to blend percentage in the TGB. This may be due to the technologies of modern CI engines being able to somewhat compensate for differences in fuel types and properties, making the overall performance of some categories like fuel consumption fairly insensitive to blend percentage in the TGB. For example, the variable geometry turbocharger vane position desired by the ECU decreased approximately 5% for a 10% increase in TGB blend ratio. Most TGBs exhibited similar performance to B100. The TGBs containing E85 had the highest fuel consumption for each blend percentage which corresponds with its lower energy content. In addition to differences in energy content, the fuel consumption may be also tied to other physical property changes, such as the higher viscosity and density for some of biofuels. R100 fuel consumption was similar to petrodiesel.

Brake thermal efficiency is also used to compare efficiency of an engine using multiple fuels. In general terms, thermal efficiency is how efficient an engine can convert the energy in the fuel into useful power. As shown in Figure 4-2, all biofuels had higher thermal efficiencies than petrodiesel. The increased lubricity of the biofuels could cause a reduction in engine friction and

improved efficiency at this load [101], with others in literature reporting a more complete combustion as compared to petrodiesel [178]. For the TGB fuels, the improvements in efficiency could also be tied to the improved spray patterns and atomization performance in combustion due to explosive vaporization of the low boiling constituents [80], [161]. Additionally, since the heating value of the biofuels is lower, more mass needs to be injected into the combustion chamber. At low load, this may be realized as improved jet penetration and air utilization [137].

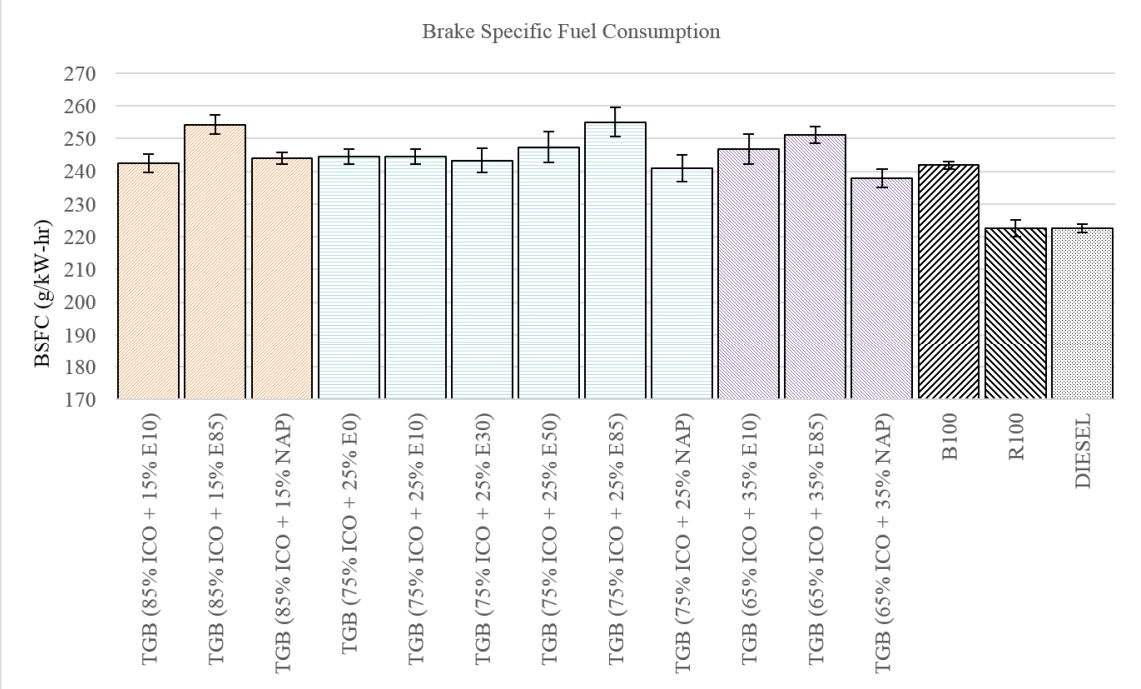

Figure 4-1. Brake specific fuel consumption.

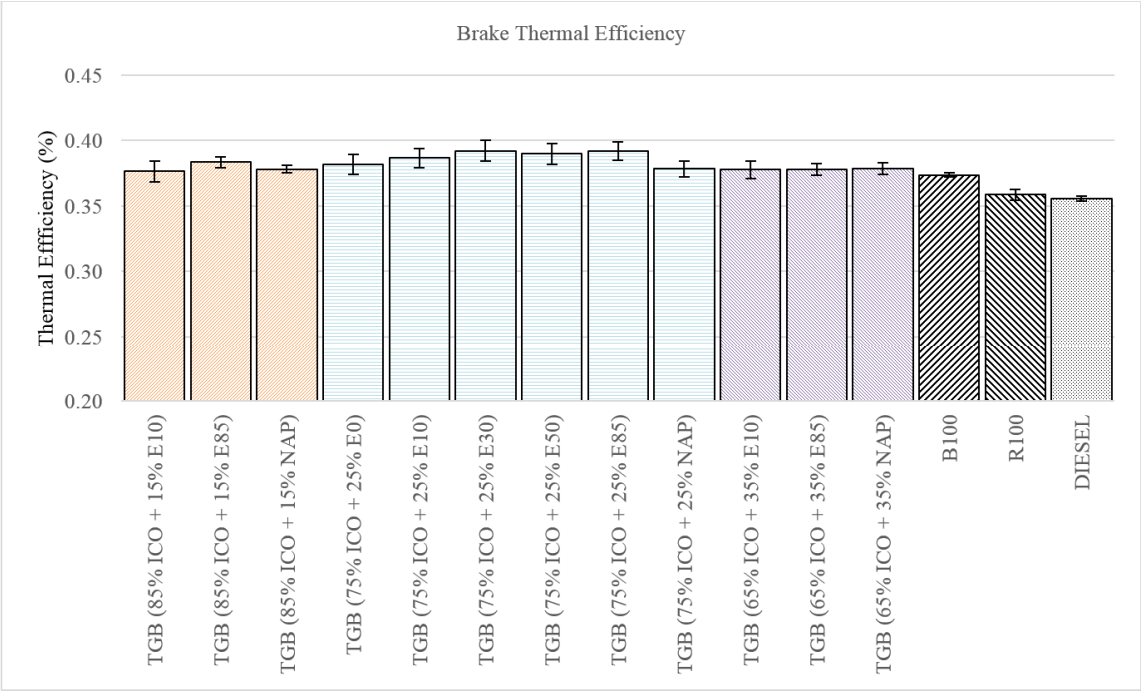

Figure 4-2. Brake thermal efficiency.

4.3.2 Brake specific emission results

Brake specific emissions (BSE) relate emission mass flow to engine loading. BSE takes into account different power levels and fuel composition. The emissions of carbon monoxide (CO) for the engine testing are shown in Figure 4-3. Both B100 and R100 showed a reduction in CO emissions compared to petrodiesel. Some TGBs had performance similar to petrodiesel, while some blends produced higher emissions. Higher ethanol content in the TGB increased CO emissions.

The emissions of oxides of nitrogen (NO_x) for the engine testing are shown in Figure 4-4. B100 showed a small increase in NO_x emissions compared to petrodiesel, which is common for biodiesel use [14], while R100 showed a reduction in NO_x as compared to petrodiesel. The 85/15 blend ratio TGBs resulted in higher NO_x emissions as compared to petrodiesel, while the 75/25 and 65/35 TGBs were comparable to each other and lower in comparison to petrodiesel. As discussed in a later section, the two higher blend ratios also produced similar heat release curves

and more similar physical properties; the differences in NO_x formation has been linked to these differences [136].

The emissions of non-methane hydrocarbons (NMHC) for the engine testing are shown in Figure 4-5. NMHC emissions for R100 and B100 were similar and slightly lower than petrodiesel. The TGBs resulted in higher NMHC emissions than petrodiesel. Higher ethanol content in the TGB also increased NMHC emissions.

Total PM mass emissions were measured gravimetrically via collection onto teflon filters. The resulting brake specific particulate matter results are shown in Figure 4-6. PM emissions from R100 and B100 were slightly lower in comparison to petrodiesel. TGB PM emissions were higher than petrodiesel with increased ethanol content also causing increased PM emissions, with a large increase for some blends. For example, TGBs formed from naphtha averaged 1.2 times the PM emissions of petrodiesel, while the 65/35 TGB mixed with E85 was 14 times higher. The higher emissions from the 65% ICO + 35% E85 blend may be a sign of phase separation in the engine fuel system, further discussed in a later section. The TGBs formed with E85 used in engine testing were soluble at room temperature, but the higher temperatures and pressures of the engine fuel system could have caused the components to begin to separate and be linked to increased emissions.

The overall trends for the emissions of volatile organic compounds (VOCs) during the engine testing were similar to the NMHC results. The FTIR groups VOCs as non-methane, non-ethane, non-aldehydes hydrocarbons below C4. B100 exhibited the lowest VOC emissions (less than 20 parts per million) and R100 also had a small reduction compared to petrodiesel. Some TGBs, like the 75% ICO + 25% E10 blend, had VOC emissions similar to petrodiesel, while some were higher depending on blend type and ratio with similar trends as the other emission categories.

VOCs can create photochemical smog under certain conditions, so it is important that biofuels have similar or reduced VOC emissions as petrodiesel [134]. The emissions of formaldehyde, hydrogen cyanide, and other hydrocarbons measured by the FTIR during the engine testing were small in concentration, with all test runs less than 5 ppm.

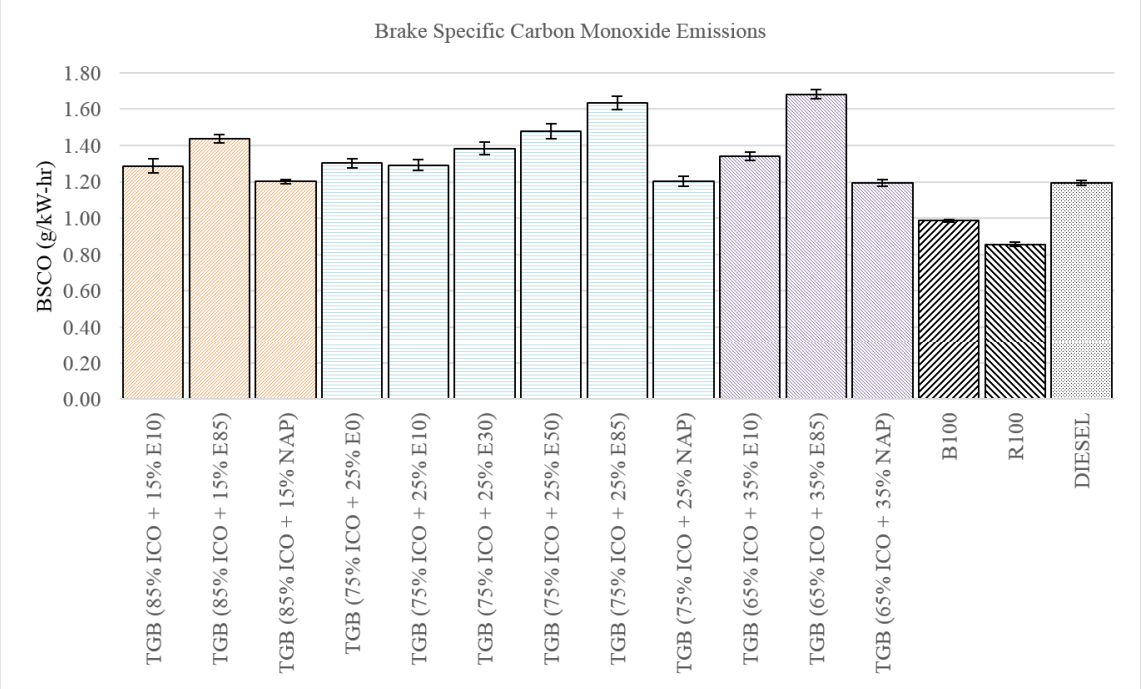

Figure 4-3. Brake specific carbon monoxide results.

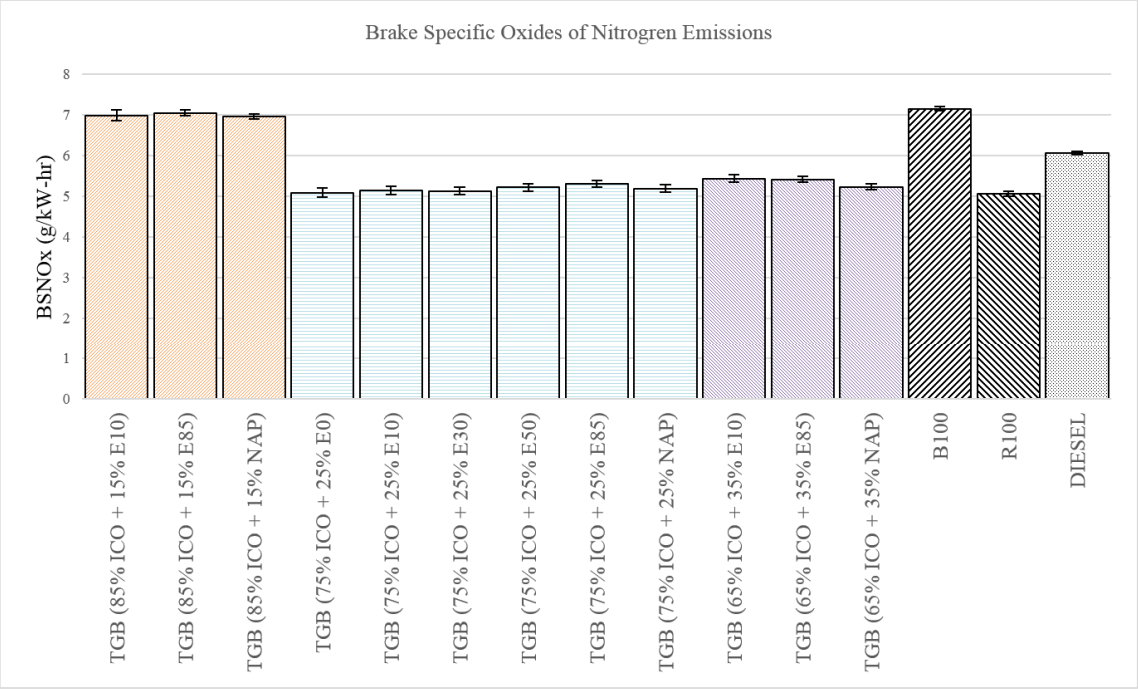

Figure 4-4. Brake specific oxides of nitrogen (NO_x) results.

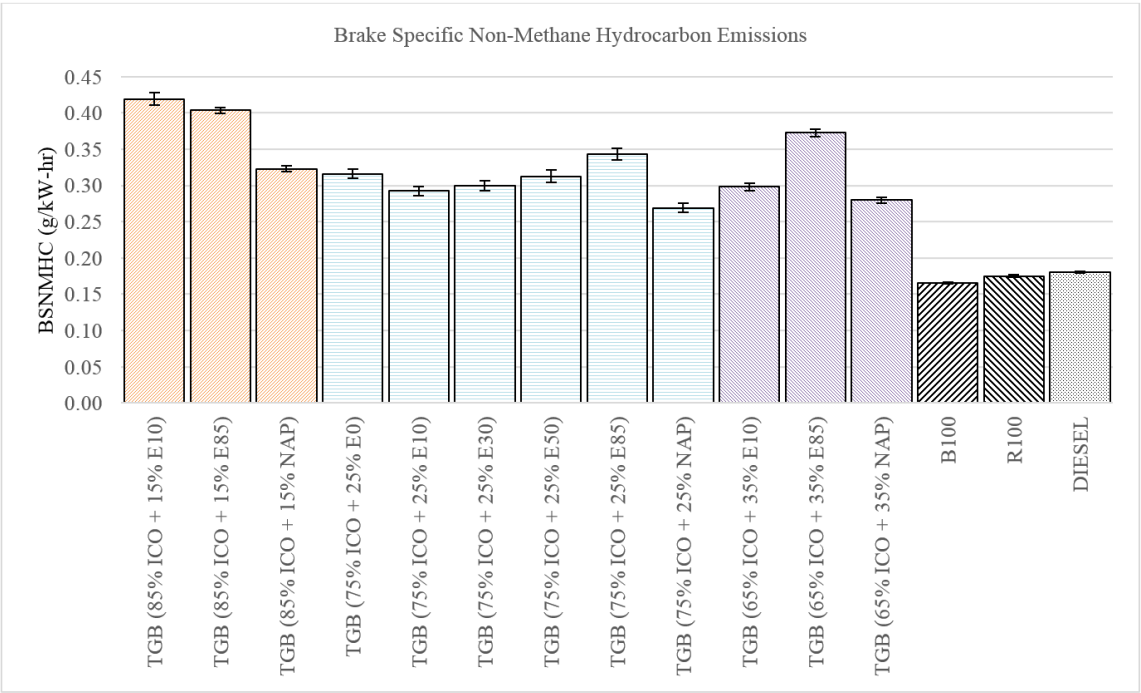

Figure 4-5. Brake specific non-methane hydrocarbon results.

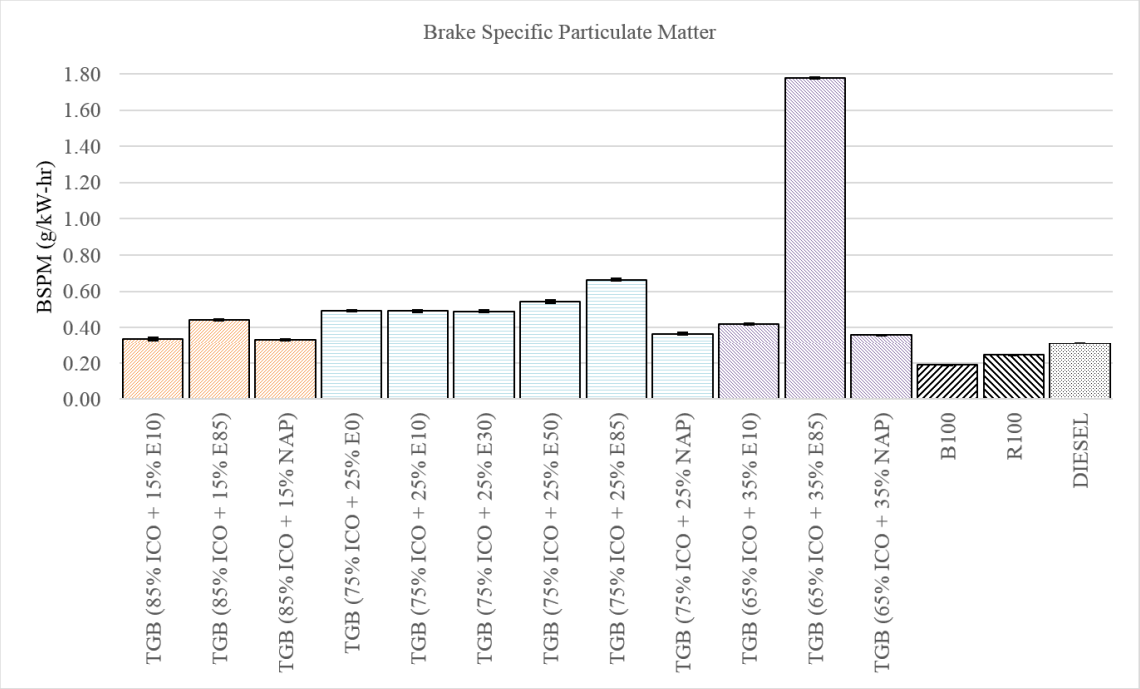

Figure 4-6. Brake specific particulate matter.

4.3.3 Heat release results

As discussed in the test setup section, a pressure transducer was used to record 1000 pressure cycles for each run. Peak pressure coefficient of varience (COV%) was less than 3% during the evaluation for each run. The subsequent heat release curves of the biofuels depicted some similarities as shown in Figure 4-7 - Figure 4-9. The peak of the heat release profile was slightly smaller for the biofuels. The blend rate did affect TGB heat release rate, with the 75/25 and 65/35 blend ratios more petrodiesel shaped than the 85/15 TGBs, although the higher blends also had more variability in their results. The 75/25 TGB profiles show the engine was fairly insensitive to ethanol content in the TGB with respect to heat release rates. The biofuels were also smoother shaped (less defined premixed and mixing controlled combustion phases) than petrodiesel. These trends were common to other combustion research comparing biodiesel to petrodiesel and are attributed to differences in energy content and other physical property differences [135], [136], [178]. Standard injection timing for this engine (single event) was used

during testing. The engine ECU uses a lookup table based on throttle position, engine speed, and engine temperatures to determine injection timing. Even though the same engine speed and torque set points were used for each run, there were small injection timing differences due to differences in physical properties of fuels. Actual start of injection (SOI) for each fuel is shown in Figure 4-10.

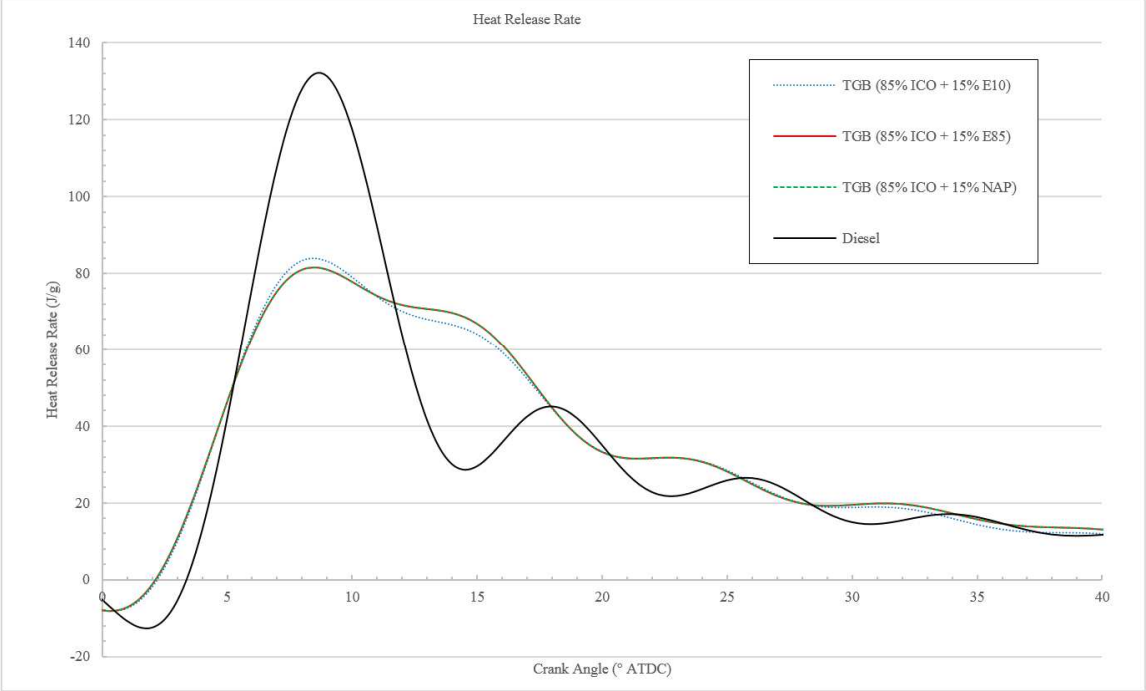

Figure 4-7. Heat release rate for TGB 85/15 fuels.

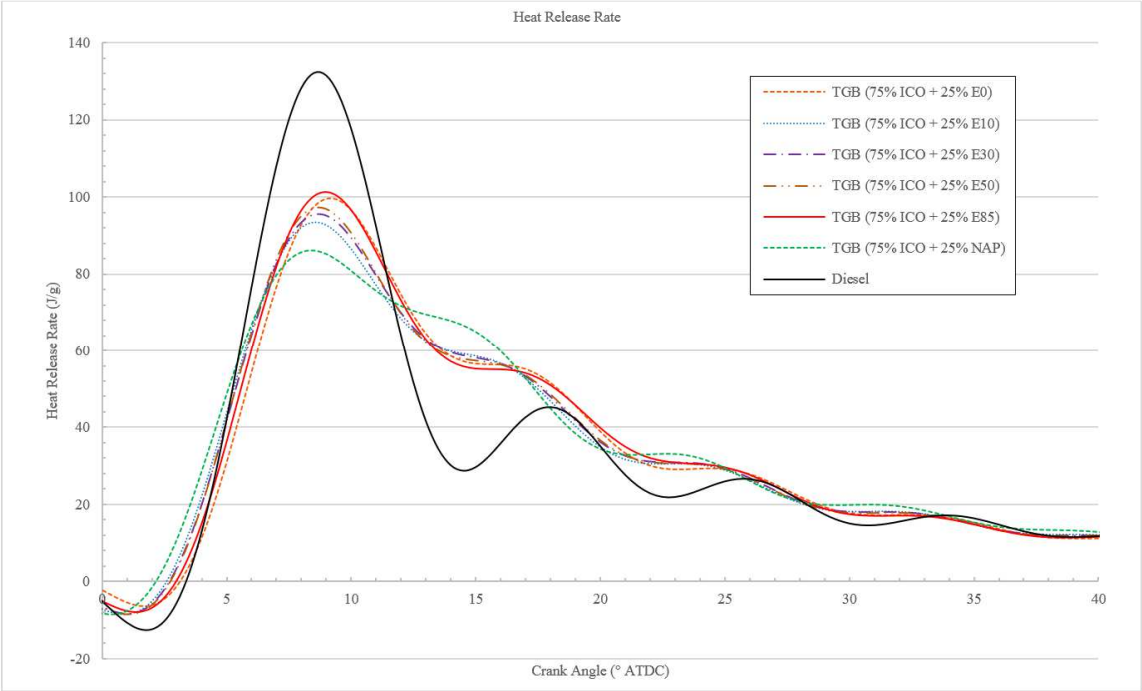

Figure 4-8. Heat release rate for TGB 75/25 fuels.

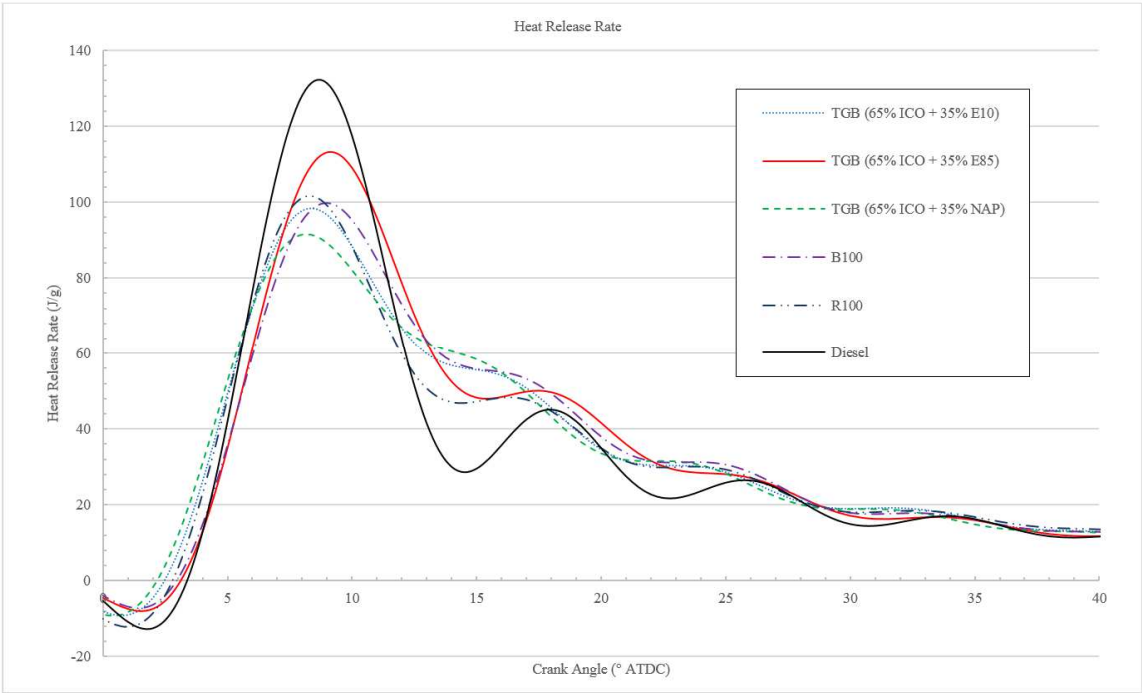

Figure 4-9. Heat release rate for B100, R100, and TGB 65/35 fuels.

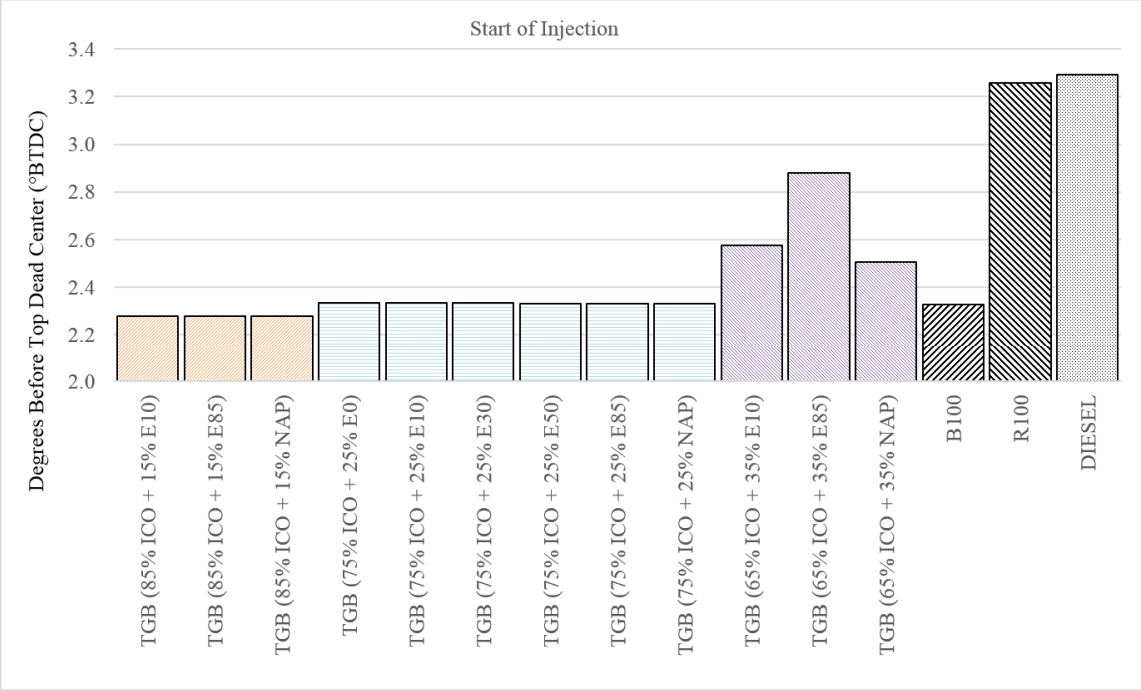

Figure 4-10. Injection timing.

4.3.4 Physical stability of TGBs

The resulting phase diagrams for TGBs made from ICO + gasoline + ethanol in Figure 4-11 show ethanol can induce phase separation in TGBs due to the differences in chemical structure of the oil and alcohol [94]. Additionally, the high polarity of water enhances the polar part in an ethanol molecule and further decrease compatibility with non-polar molecules [148]. The 1% by mass water content tested here is the maximum allowed by ASTM standard for gasoline-ethanol blends and should represent the worst-case scenario for those blend components [149]. However, additional water can also be introduced from the vegetable oil; the ICO used for this study had 0.65% water content. Changes in temperature also further decreased component compatibility over room temperature. At the lower temperature, some TGBs with high vegetable oil content began to crystalize or gel. The phase diagrams for TGBs made from ICO + renewable naphtha, shown in Figure 4-12, did not have any separation.

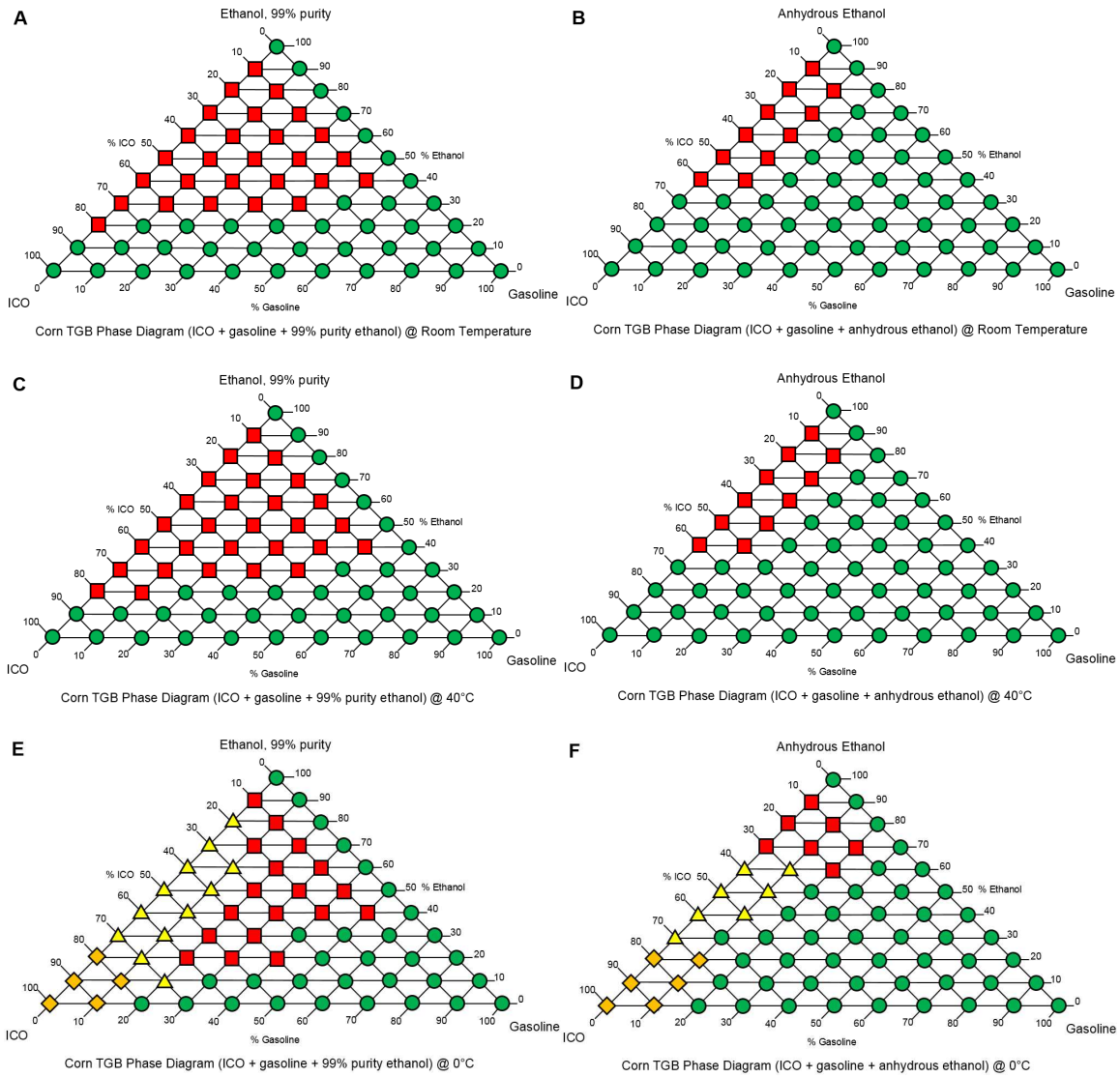

Figure 4-11. TGB phase diagrams (ICO + anhydrous/99% purity ethanol + gasoline) @ room temperature (A, B), 40 °C (C, D), and 0 °C (E, F).

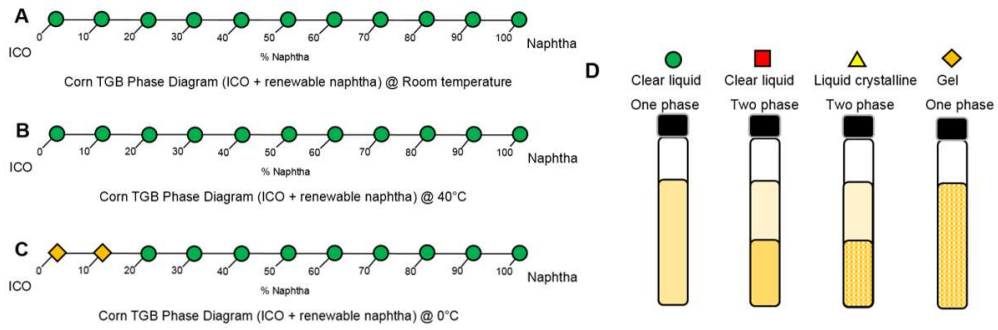

Figure 4-12. Corn TGB phase diagrams (ICO + renewable naphtha) @ room temperature (A), 40 °C (B), 0 °C (C), and phase diagram legend (D).

4.3.5 Chemical of TGBs

Figure 4-13 shows the ^{1}H NMR spectra for corn SVO, E10, and corn TGB overlaid. TGBs did not show any chemical changes upon blending, and were simply a sum of their constituent parts. There was no evidence of chemical changes that could produce sediments or otherwise degrade the fuel. The proton resonances of the triglyceride fatty acid chains and glycerol backbone of the corn oil correspond to what has been reported in the literature [155], with olefinic protons of unsaturated fatty acids resonating at 5.3-5.5 ppm, glycerol protons resonating at 5.26, 4.1 and 4.3 ppm, methylene protons of polyunsaturated and unsaturated acyl chains at 2.78 and 2.05, protons of acyl moieties in triacylglycerols at 2.3 and 1.6 ppm, methylene envelope protons at 1.2 ppm, and methyl protons of polyunsaturated acids at 0.91 ppm, and of saturated and unsaturated acids at 0.88 ppm. The proton resonances of aromatic (6.7-8.0 ppm), olefinic (4.6-6.0 ppm) and aliphatic (0.5-3.3 ppm) hydrocarbon protons in the E10 corresponded to those reported for gasoline and ethanol (multiplets around 3.7 and 1.3 ppm) [152]. The results in Figure 4-13 are for the 75/25 TGB with the other blend ratios tested having similar results. Previous NMR research using carinata TGBs also found chemical stability upon blending, and additionally no chemical changes after one year of storage [179]. Clear chemical changes were found due to transesterification (B100) and hydroprocessing (R100), as shown in Figure 4-13 and also described in Drenth et al [179] for the carinata fuels.

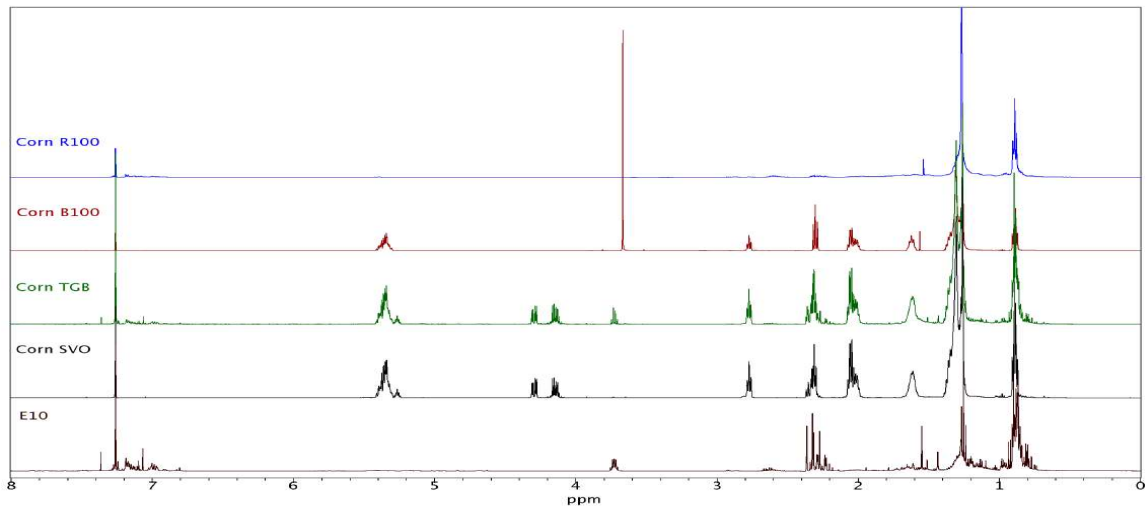

Figure 4-13. Corn TGB NMR results.

4.3.6 Fuel property results

One benefit to TGBs is fuel properties can be somewhat tailored depending on the blend type and ratio. TGB fuel properties (SVO + E10 blends) were recently studied in detail, with results for viscosity, density, speed of sound, heating value, flashpoint, cold flow properties, and lubricity [179]. The results of the fuel properties measured during this study were similar, and are shown in Table 4-3 for the fuels used in engine testing. A brief discussion follows for the viscosity and cold flow properties, and includes important findings from the addition of E85 and naphtha as TGB blend agents.

Viscosity is one of the most important fuel properties; high viscosity fuels are linked to both short-term engine performance issues such as startability and longer-term issues such as coking of injectors [93]. E10, E85, and renewable naphtha all reduced viscosity at approximately the same rate as blend percentage was increased, as shown in Figure 4-14. Figure 4-14 also shows TGBs are more effective at reducing viscosity than by mixing vegetable oil with petrodiesel (dilution method). For reference, the acceptable range for kinematic viscosity by ASTM standard for B100 fuels @ 40 °C is 1.9-6.0 mm^2/s and for Grade No. 2-D S15 petrodiesel @ 40 °C is 1.9-4.1 mm^2/s [100], [147]. As was the case with previous research, changes in lower heating value

(LHV) were approximately linear with changes in blend ratio depending on the energy content of the blend component. TGB cold filter plugging point (CFPP) causes large reductions as a small amount of blend is added to the vegetable oil (~5%), then tapers off for higher blend ratios as shown in Figure 4-15. Like viscosity, the E10, E85, and naphtha blends give greater reductions to CFPP than the dilution method. One important observation made when cold flow testing was the TGB made with higher levels of E85 separated during the cold flow test. The blends were soluble at room temperature, but as the blend decreased in temperature, the components would separate. This explains why the CFPP did not continue to decrease with higher blend ratios the way the TGBs made with E10 and naphtha did.

Table 4-3. Physical properties of fuels used in engine performance testing.

FUEL TYPE	Ethanol Content %	Density @ 20° C (g/cm3) *Anton Paar DSM5000*	Kinematic Viscosity @ 40° C (mm2 s-1) *Anton Paar SVM3000*	Lower Heating Value J g^{-1} *IKA C200*
PETRODIESEL	0	0.8416	2.324	44963
TGB: 85% Corn Oil + 15% E10	1.5	0.8759	13.774	38669
TGB: 85% Corn Oil + 15% E85	12.75	0.8849	14.700	36936
TGB: 85% Corn Oil + 15% NAP	0	0.8822	15.514	39032
TGB: 75% Corn Oil + 25% E0	0	0.8550	7.705	39307
TGB: 75% Corn Oil + 25% E10	2.5	0.8561	7.724	38922
TGB: 75% Corn Oil + 25% E30	7.5	0.8642	8.134	38152
TGB: 75% Corn Oil + 25% E50	12.5	0.8740	8.420	37381
TGB: 75% Corn Oil + 25% E85	21.25	0.8813	8.647	36033
TGB: 75% Corn Oil + 25% NAP	0	0.8723	10.311	39527
TGB: 65% Corn Oil + 35% E10	3.5	0.8490	4.905	39175
TGB: 65% Corn Oil + 35% E85	29.75	0.8656	6.157	35131
TGB: 65% Corn Oil + 35% NAP	0	0.8566	6.959	40022
B100	0	0.8755	5.407	39420
R100	0	0.8174	1.824	44820

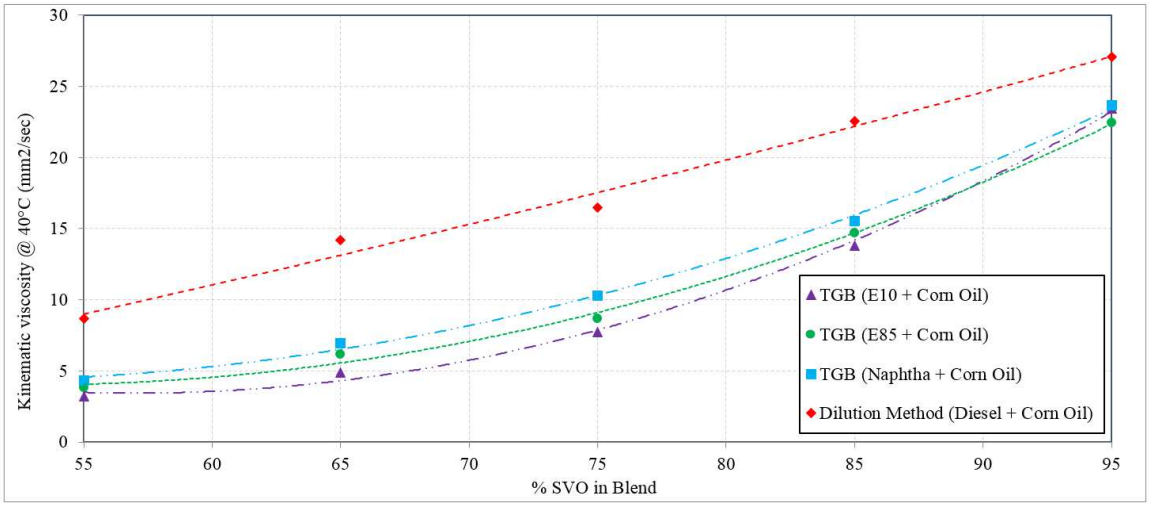

Figure 4-14. Viscosity versus % corn oil in blend.

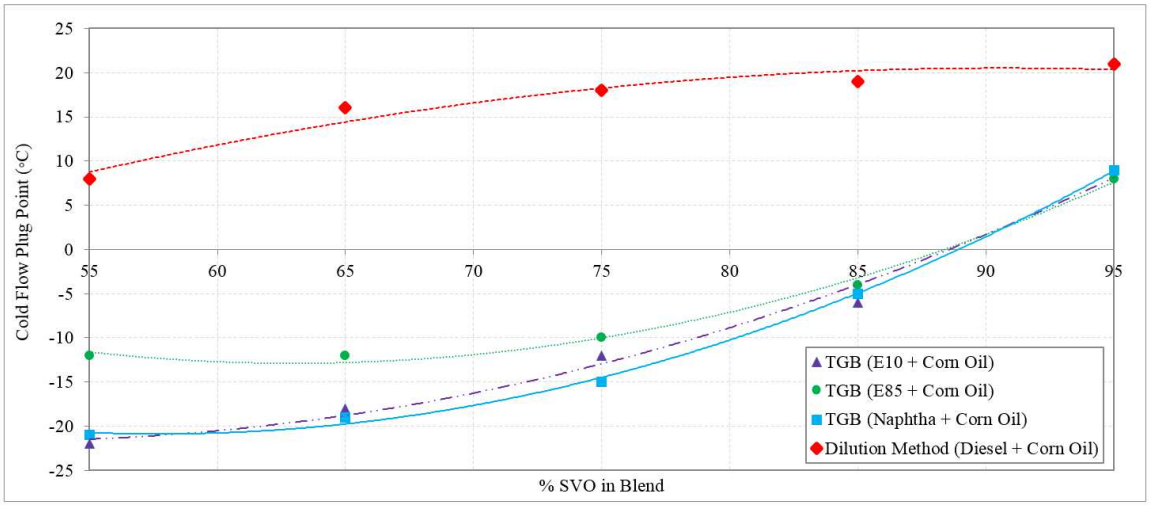

Figure 4-15. Cold Filter Plugging Point (CFPP) versus % corn oil in blend.

4.4 Conclusions

The use of ICO from a local ethanol plant combined with the TGB fuel pathway offers farmers a simple alternative for producing and using biofuels on-farm. Based on this research, some specific observations and conclusions about TGB blend components and ratios emerge. The study showed a modern agricultural petrodiesel engine was compatible with TGBs at the three ratios tested without modification. However, the 75/25 and 65/35 blend ratios performed better in some categories as compared to the 85/15 TGBs. This is likely tied to differences in fuel properties, especially the reduced viscosity for the higher blends. In addition to the blend ratio,

TGB blend component also showed some differences. High ethanol content in the blend (using E50 and E85) caused higher emissions in the test engine at the speed and load used in the test. Additional engine testing at other loads could better quantify ethanol's effect on emissions; other research has found some emission benefits from ethanol blending in diesel engines are not realized until higher loads [148]. Another potential issue with using TGBs formed from high E# gasoline is the possibility of component separation, especially if water content of the components is not known. Unless water content can be assured, it is recommended that users of TGBs limit ethanol content in the gasoline portion of the blend to 10% (E10) to ensure no TGB phase separation over a wide temperature range. TGBs formed from renewable naphtha had favorable results. Naphtha blends showed a similar reduction in viscosity as using gasoline to form TGBs, but were cleaner burning for all emission categories tested. In addition, naphtha does not have any solubility issues inherent to the blends containing ethanol. Finally, a TGB formed from ICO + renewable naphtha is 100% renewable.

B100 performance was also favorable with reductions in emissions as compared to diesel in every category except NO_x. B100, whether produced on farm-scale or produced commercially, might be preferential over TGBs for farmers looking to use biofuels but primarily operating newer machinery still under warranty. R100 performance was similar to petrodiesel in fuel consumption, yet had emission benefits over petrodiesel in several categories. The R100 pathway offers a true "drop-in" alternative to petrodiesel that is desired by the military and other users.

TGBs formed from ICO feedstock allow farmers a simple yet effective method to produce on-farm fuel that can improve sustainability in agriculture. Mixing TGBs may be preferred by farmers who are disinclined, either financially or technically, to produce and utilize biodiesel at their operations. Several lessons were learned about TGBs that can be implemented and applied

to future research. Future research should also use long-term durability testing to assess the impact of using TGBs in the combustion chamber, fuel system, and after-treatment components.

Chapter 5. TRIGLYCERIDE BLENDS (TGBs) AS AN OPTION FOR ON-FARM FUEL PRODUCTION[4]

5.1 Quick facts…

- A Triglyceride Blend (TGB) is a biofuel pathway that is easy and economical to produce.
- As compared to straight vegetable oil (SVO), TGBs improves viscosity, cold flow performance, and other physical properties to levels more similar to petrodiesel without the need for a fuel heater.
- TGBs may be well suited to on-farm production of fuel for diesel engines, and would allow the use of oilseeds that may not have a nearby commercial market.
- There are disadvantages to using TGBs, particularly warranty and safety concerns that need to be understood by potential users.

5.2 Purpose and disclaimer

The purpose of this fact sheet is to provide information about Triglyceride Blends (TGBs), the resultant product of mixing straight vegetable oil (SVO) with E10 gasoline as a thinning agent. The fact sheet is a way to share information and key findings with interested parties in an easy to understand and more accessible manner than technical publications. No ASTM standard exists for TGBs and the use of TGBs may void new engine warranties. Consult local and regional laws for off-road fuel production for agriculture use. Any use of this fuel production method is an assumption of risk; Colorado State University (CSU) is not liable for any damages, losses or causes of action of any nature.

[4] Published as a *CSU Extension Fact Sheet, Farm and Ranch Series* by A.C. Drenth et al. [201]

5.3 What is a TGB?

Straight vegetable oil (SVO) has been used as a fuel in diesel engines since their inception when Rudolph Diesel advocated vegetable oil fuels, hoping that farmers could supply their own fuel through oilseed cropping. However, in modern unmodified diesel engines, most experts agree that long-term use of SVO can cause problems that may decrease service intervals and reduce engine life. Many of these problems are tied to the high viscosity of SVO, which is typically 10-20 times greater than petrodiesel. Viscosity can be lowered through several methods, which are referred to as fuel conversion methods or fuel pathways. Among the more common biofuel pathways are those using chemical reactions. For example, biodiesel is produced through the transesterification of vegetable oils (or animal fats) into mono-alkyl esters of long chain fatty acids. Making biodiesel entails a controlled chemical reaction using an alcohol and a catalyst. As an alternative, TGB for biofuel is made through a physical, not chemical, conversion process. TGBs are made by mixing vegetable oil (triglycerides) with gasoline or other low viscosity fuel and using the resulting solution (blend) as a petrodiesel substitute. The reduction in viscosity through this blending process allows TGBs to be used in diesel engines without modification. The addition of gasoline will also increase the energy content of TGBs compared to SVO, which increases fuel economy and can increase engine performance parameters like maximum power [97]. Some U.S. farmers have been using TGBs successfully for several years (with various naming conventions for this biofuel [180], [181]), and the Engines and Energy Conversion Laboratory (EECL) at CSU has been conducting research on this pathway since 2010. The main advantage of TGBs are: they are economical, fast to make, and relatively easy to make. TGBs are produced with low energy inputs, and do not create waste products or require a catalyst. Cost of production and initial capital investment are

relatively low, making economy-of-scale of less concern than other biofuel production options. Due to the ease of production, TGBs may be well suited to on-farm fuel needs in rural areas. TGBs may also be relevant to farmers looking to grow a nontraditional oilseed crop that may work well in their rotation, but does not have a commercial market established in their area. This would create a use for oilseeds produced as cover crops, off-season crops, relay crops, fallow-substitutes, or in other rotations that could be planted in concert with water rights leasing.

5.4 TGB production

A basic TGB production flow diagram is shown in Figure 5-1 and is described below in four steps:

- **Step 1**: The starting point to make TGBs is virgin vegetable oil. The focus of this fact sheet is not on the on-farm crushing of oilseeds, with several other resources already dedicated to that topic (e.g. references [182] and [183]). Alternatively, some farmers may be able to readily obtain oil from a commercial source, such as a nearby oilseed processing facility or ethanol plant. The EECL has not done research on other sources of feedstock for TGB production, such as used cooking oil or animal fats.
- **Step 2**: After extraction, an initial filtering of the oil is typical to remove residual meal particles. There are other references available (e.g. reference [184]) for additional details on filtering oil. The initial and final filtering steps shown in Figure 5-1 are for illustration purposes and other combinations or methods may be acceptable. Regardless of method, the importance of filtering cannot be overlooked. Poorly filtered TGBs will clog fuel filters and may reduce engine longevity.
- **Step 3**: Once the vegetable oil is extracted and filtered, the blending agent is added.

- **Blending Agent** - The EECL has used gasoline with ethanol contents ranging from E0 to E85 during TGB testing, as well as renewable naphtha. When using gasoline as a blending agent, the recommendation is to limit ethanol content to 10% (E10). Higher levels of ethanol in the blend could cause component separation due to differences in chemical structure of the vegetable oil and alcohol [179]. Engine performance was favorable when using renewable naphtha as a blending agent, but this fuel has limited availability compared to gasoline. For simplicity, the remainder of this document refers to the blending agent as E10.
- **Blending Agent Percentage** - Short-term engine performance testing at the EECL using a direct injection, common rail, diesel engine was carried out using SVO to E10 volumetric ratios ranging from 100/0 to 20/80. EECL testing showed diesel engines are fairly insensitive to the blend ratio of TGBs, although performance degrades with high (>50%) and low (<15%) E10 contents [185]. The recommendation for best performance is to use volumetric ratios between 15-35%. As shown in Figure 5-2, the viscosity is greatly reduced with a small amount of E10, and the benefit to viscosity tapers off above ~35% blend ratios [179]. All figures in this document show the average value for seven oils: camelina, canola, carinata, corn, pennycress, soy, and sunflower.
- **Blending Technique** - The desired blend ratio between vegetable oil and the thinning agent can be achieved in two different ways. As was done in EECL testing, a known volume of SVO (e.g. 15 gallons) was blended with a known volume of E10 (e.g. 5 gallons) to make a 75/25 volumetric ratio. In practice, some farmers using TGBs and mixing them in bulk find a gravimetric approach more

convenient; using a hydrometer to control how much E10 is added to the SVO [97]. For the hydrometer method, E10 is added to SVO progressively until the resulting blend "floats" the hydrometer at a pre-determined level (e.g. SG ≈ 0.87). A hydrometer is an instrument that measures specific gravity (SG), which is the ratio of the density of a fluid to the density of water. Fuel property testing of TGBs has shown density varies approximately linearly with blend ratio as shown in Figure 5-3, making using a hydrometer (Figure 5-4) an effective approach [179]. Since density of vegetable oil increases with decreasing temperatures, more E10 is needed to achieve the same SG in the winter months than shown in Figure 5-3 (measured at room temperature). Farmers should be also be aware the physical properties of vegetable oil can vary by region, and those produced on their farm may differ from what has been used in EECL testing.

- **Step 4**: Once the desired ratio of SVO to E10 is achieved, the TGB should be agitated to ensure adequate mixing. TGBs do not require large amounts of agitation to form a solution, but hand or mechanical mixing ensures homogeneity. Due to the volatility of the gasoline component, this mixing process can increase the pressure in a sealed container, and thus should be outgassed (vented) before storage.
- **Step 5**: A final filtration of TGBs to 1 micron after the blending process is recommended before use. The final TGB can be used in neat form or, similar to biodiesel (i.e. B20), can be mixed with petrodiesel to provide a good balance of cost, emissions, cold-weather performance, materials compatibility, and ability to act as a solvent [186]. EECL testing has shown TGBs (SVO + E10) are both physically stable (do not separate) and are chemically stable over the expected timescale of use [179]. Operators should still try to

minimize storage time, as TGBs contain oxygen and can degrade, undergoing rancidity with long term or improper storage.

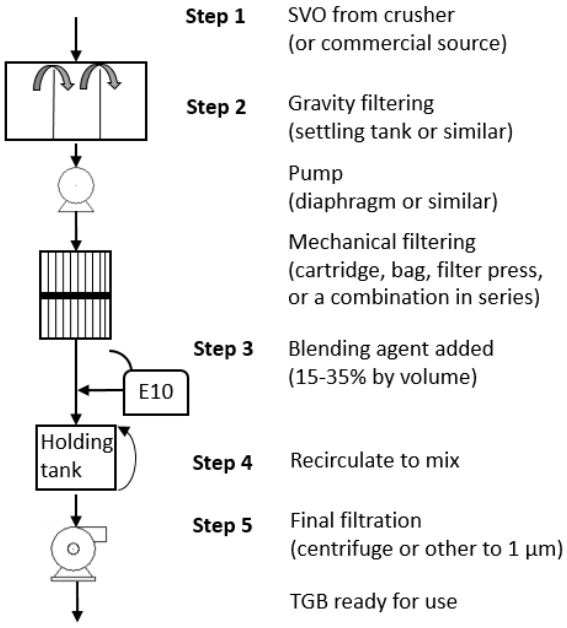

Figure 5-1. TGB production.

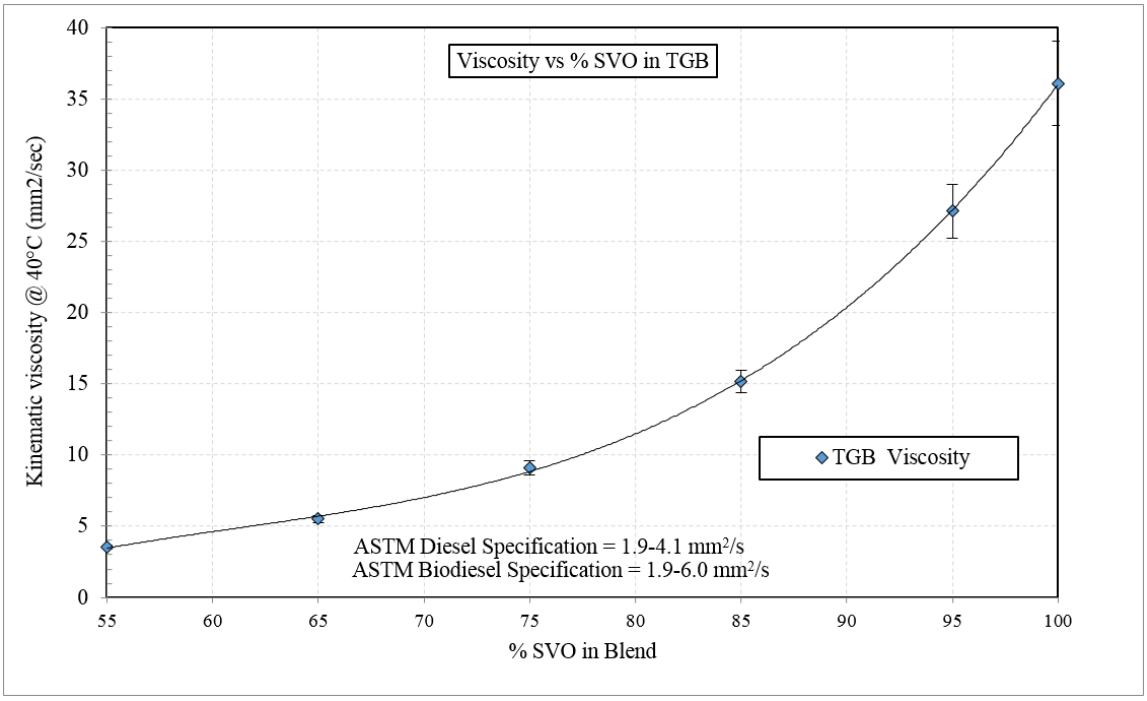

Figure 5-2. TGB viscosity versus blend ratio [179].

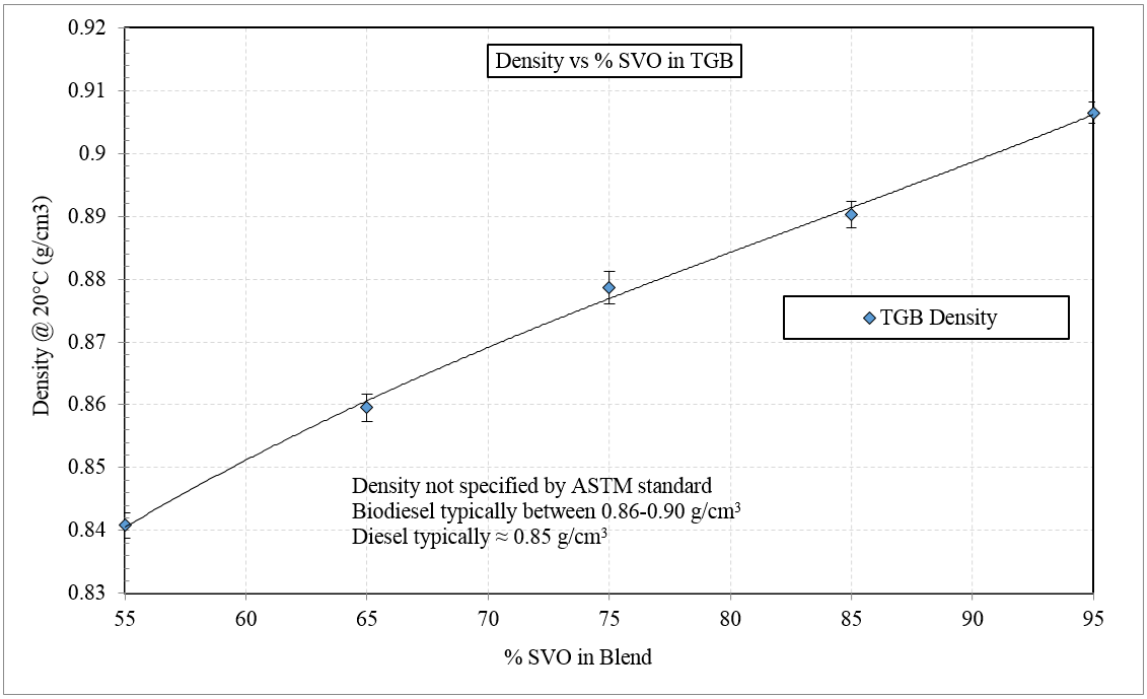

Figure 5-3. TGB density versus blend ratio [179].

Figure 5-4. Hydrometer.

5.5 Engine performance and durability

Engine performance has been generally acceptable for the TGBs discussed above. As shown in Figure 5-5, most categories (fuel consumption, thermal efficiency, carbon monoxide

emissions, and oxides of nitrogen emissions) were within ±10% of petrodiesel performance with slightly higher hydrocarbon and particulate matter emissions at the tested load and speed [137]. Engine durability is the testing of longer term effects of TGBs. Durability testing at the EECL is performed using a single cylinder, direct injection, diesel engine over extended intervals. Durability issues include oil degradation, combustion chamber carbon build-up, and fuel system compatibility. At the conclusion of the durability test interval, the engine is disassembled for post-test inspection of the injector and combustion chamber. Engine durability under TGB usage is an area of ongoing research at the EECL. Initial results show TGBs have significantly less carbon build-up on the injector and combustion chamber than when using SVO of the same feedstock over the same interval. Biodiesel exhibited less carbon build-up than a TGB (90/10 blend), and petrodiesel. For the testing, biodiesel and TGB were produced from the same canola oil feedstock [187]. Figure 5-6 shows a relative comparison from some of the fuels evaluated for durability.

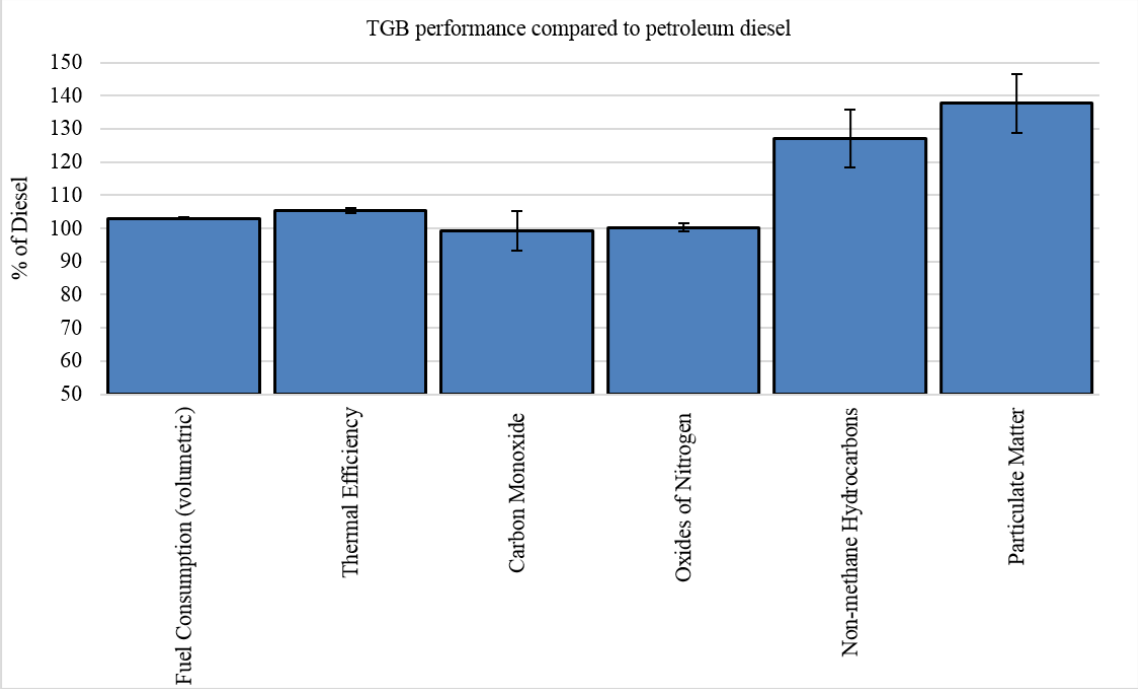

Figure 5-5. TGB (75/25 blend) engine performance, John Deere 4.5L PowerTech (Tier 3 compliant) at 1700 rpm and 250 N-m [179].

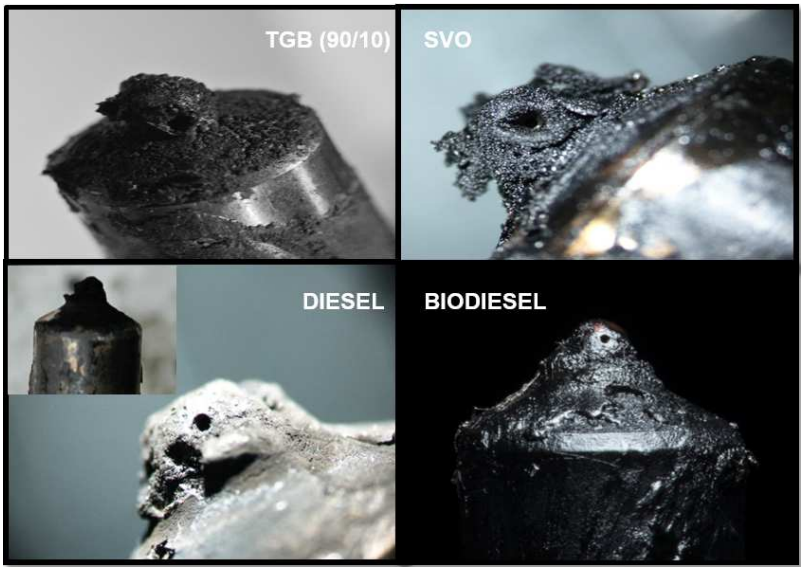

Figure 5-6. 300-hour durability results of canola biofuels, Yanmar 0.76L TF140E at 1800 rpm and 4.5 kW [187].

5.6 Safety considerations

Low volatility has been linked to poor atomization and combustion of SVO in diesel engines. In addition to the viscosity reduction, making TGBs (adding E10) also improves the volatility compared to SVO. A downside to this increased volatility is a corresponding reduction in flash point. Flash point is the lowest temperature at atmospheric pressure at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions. The volatility of the E10 causes TGBs to have low flash points in neat form due to the low flash point of the gasoline (~-40 °C) and ethanol (~13 °C) components. For reference, the ASTM specification for biodiesel flash point is 93 °C minimum while petrodiesel is 52 °C minimum. Testing at the EECL has shown even a small amount of E10 (<5%) in a TGB will drive the flash point to a low value (<40 °C). Flash point, as specified by the ASTM standards, is not directly related to engine performance. It is, however, of importance in connection with legal requirements and safety precautions involved in fuel handling and storage that are normally specified to meet insurance and fire regulations [100].

Related to flash point are flammability limits in a fuel tank headspace. As the temperature rises in a fuel container, fuel vapors are produced and mix with air which progress from too-lean-to-burn, to combustible, to too-rich-to-burn. Quantifying flammability of TGBs is an area of ongoing research at the EECL. Initial flash point and vapor pressure studies have shown that TGBs have similar flammability to neat gasoline. These findings are similar to the research of others on diesohol (petrodiesel + ethanol) and other biofuel blends containing ethanol (i.e. biodiesel + ethanol) because the flammability is dominated by the high volatility component. Besides temperature, the flammability limits of gasoline depend on several factors such as fill ratio, winter or summer blend, ethanol content, and are therefore difficult to summarize here. Published data showed the vapor above the fuel level in a gasoline storage container at normal ambient temperature exceeds the upper flammability limit (too-rich). The approximate flammable range for summer E10 (1/30 fill ratio) is from -48 to -16 °C [188].

Flash point testing results indicates that, according to definitions by the National Fire Protection Association (NFPA), U. S. Department of Transportation (DOT), and U. S. Occupational Safety and Health Administration (OSHA), TGBs should be treated as a Class I (flammable) liquid as they have flash points below 100 °F (37.8 °C), while petrodiesel fuel is a Class II (combustible) liquid. Like other petrodiesel fuel substitutes that contain a high volatility fuel component, TGB handling, storage, and dispensing must be afforded the same cautions as neat gasoline (treated as a Class I liquid). Depending on the application, additional safety measures may be warranted for using TGBs, such as the fitting of flame arresters on fuel tanks [188], [189].

5.7 Other observations

Like biodiesel, farmers using TGBs have reported some solvent properties that can break down the varnish deposits left by petrodiesel on the walls of the existing fuel storage tanks or fuel systems [186]. The breakdown of these deposits could be significant in older machinery, which can cause fuel filters to plug rapidly during the initial transition to biofuel use. Once the contaminant is removed from the fuel system, subsequent fuel filter service intervals should return to normal.

Also like biodiesel, users of TGBs have reported quieter and smoother sounding engine operation at some loads compared to petrodiesel. Other researchers have linked this effect to the increased cetane number and lubricity of biodiesel. The EECL has not done cetane number testing on TGBs, but have noted injector timing and combustion heat release rate curves are similar for TGB (75/25 blend) and biodiesel [137]. One advantage to mixing SVO or biodiesel with ultra-low sulfur diesel (ULSD) is the biofuel improves the lubricity, even at low blend ratios (i.e. B2). Initial lubricity testing of a 75/25 TGB shows it also has inherent lubricity, and the E10 is not negatively affecting lubricity at that ratio [179].

5.8 Conclusions

TGBs may help fill a niche role in farm-fuel production or other remote users. TGBs allow farmers a simple yet effective method to produce off-road fuel that can improve sustainability in agriculture. TGBs may be well suited for farmers who introduce an oilseed crop into their rotation, but do not have a nearby commercial market for the crop. Farm-fuel production also offers some protection from price volatility of petroleum fuels, and an option to produce their own fuel in times of fuel shortages. Operators of newer equipment should consult warranty

statements before using TGB fuel. The flammability concerns outlined above also must be well understood and mitigated by potential users.

Chapter 6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Introduction

This chapter provides overall conclusions and recommendations from this research.

6.2 Feedstock conclusions

6.2.1 Camelina, carinata, and pennycress industrial oilseeds

The industrial oilseeds discussed in this report grow well in the U.S., are compatible with existing agriculture and fuel infrastructure, and have potential to see widespread adoption in the near term. These oilseeds, teamed with new cropping systems, show great promise to increase the quantity of biofuel production on existing farmland.

Department of Defense (DOD) officials have said that any alternative fuels for DOD operational use must be derived from a non-food crop feedstock [18]. The USAF has also identified the use of efficient and abundant non-food source biofuels as a game changing technology in energy generation for 2011-2026 [190]. Recent analysis by the USDA found using non-food feedstocks by the U.S. transportation sector can result in less direct impact on commodity markets, livestock feed, and food markets [191]. Clearly, there will be a demand for these non-food oilseeds in the near future from both the DOD and transportation sector. The use of these oilseeds for on-farm fuel can bridge the gap until the larger-scale markets mature. Due to the low input requirements of these crops, the economics may be more favorable than traditional feedstocks for farmers to produce their own on-farm fuel.

The engine performance of camelina, carinata, and pennycress-based biofuels was similar to the traditional oils in this study. There were no performance or emission categories that would preclude their use on a wider scale.

The fatty acid profiles of these industrial oilseeds differ from traditional oils like soy and rape; these differences can create difficulties meeting certain parameters of the current biodiesel standards (ASTM D6751 & EN 14214). Potential issues have been noted for camelina in two recent biodiesel conversion studies, with camelina biodiesel not meeting ASTM D6751 standards for cetane number, distillation temperature, and oxidation stability, which is in part due to its high polyunsaturated fatty acid content, and was suggested as serious drawbacks for camelina as a biodiesel feedstock [51] [115]. However, this engine performance study found no engine operability, performance, or emissions issues when using camelina fuels or significant differences from the other feedstocks. The cetane number was not measured in this report, but when using camelina based fuels there were no combustion quality issues found during the analysis of heat release curves, no evidence of knocking, nor increased gaseous and particulate exhaust emissions due to incomplete combustion. The iodine value (IV), a measure of the degree of unsaturation, is another parameter found higher for camelina biodiesel than the EN 14214 standard limit. ASTM D6751 standard does not contain an IV specification, but some engine manufacturers have suggested using B100 with a high iodine value tends to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves [192]. Longer-term performance and durability testing of camelina-based fuels will add to the data collected here. The issues outlined by these researchers could be partially mitigated by cetane and antioxidant additives. Camelina could also be blended with other esters to form a B100 that meets ASTM D6751. In future years, plant scientist may be able to reduce the high degree of unsaturation and the molecular weight of camelina oil with genetic engineering or conventional plant breeding [51].

Other researchers have also found the oxidative stability of pennycress biodiesel is acceptable according to the limit contained in ASTM D6751, but not EN 14214 which is more restrictive [65]. Carinata biodiesel has also been found to have higher viscosity and iodine value than allowed by EN 14214 [193]. Like camelina, in the short term these issues for pennycress and carinata can be mitigated through additives and by blending, and may be able to be eliminated in the future by plant scientists' breeding and genetics programs.

In some categories, the industrial oilseeds outperformed the conventional oils. For example, pennycress' biodiesel cold flow properties were superior to all other oils by approximately 10 °C. With a cold filter plugging point result of -18 °C, the feedstock has great potential in the upper Midwest. Currently, the cold flow properties of soy and other traditional feedstocks limit its use in the winter months. For example, the mandated use of biodiesel in Minnesota is lowered from B10 to B5 for the colder weather months of October through March [16]. Using pennycress biodiesel may allow Minnesota and other northern states to maintain the same blend requirement year-round.

Carinata and pennycress also have a higher percentage of very long-chain fatty acids (VLCFAs) with chain length of 20 carbon (C20) or more, than the other oils which can improve fuel conversion rates and has a wide variety of industrial uses [53]. For example, the eurcic fatty acid (C22:1) measured in this study was nearly 40% for carinata and 37% for pennycress, while the traditional oils were near 0%.

6.2.2 Industrial corn oil

Like the other industrial oilseeds, the use of industrial corn oil for on-farm fuel production has great promise. During engine testing there were no performance or emission categories that would preclude their use on a wider scale. The corn oil study also provided important lessons

learned about the engine performance of TGBs for different blend ratios and for ethanol contents within the blend. The 75/25 and 65/35 ratios had more petrodiesel like performance than the 85/15 blends. Higher ethanol within the blend (E50-E85) caused increased emissions in some categories. Additional engine testing at other loads could better quantify ethanol's effect on emissions; other research has found some emission benefits from ethanol blending in diesel engines are not realized until higher loads [148]. Although using higher ethanol contents might have economic and renewability benefits over using E10 gasoline to form corn TGBs, the increased emissions, additional safety concerns due to its flammability limits, and solubility concerns are all issues outlined in this research.

Sourcing the corn oil from an ethanol plant has several benefits over other commercial sources (crushing facilities) and other on-farm options (on-farm extraction of traditional oilseed). If corn oil is sourced from an ethanol plant, the hardware, labor, and cost of oil extraction can be avoided. Industrial corn oil will typically be more economical than soybean, canola, sunflower or similar oils obtained from a local crushing facility since those oils can also be marketed as edible oils. A farmer using industrial corn oil can produce biofuel on farm without having to grow a traditional oilseed, a crop they may not be familiar with growing. Additionally, a farmer can produce biofuel without having to use the resulting meal, which opens the door for crop farmers who do not own livestock.

Nearly ten years after the passage of the RFS, many U.S. farmers now have an ethanol plant in relatively close proximity. Figure 6-1 overlays the major corn producing areas of the U.S., the most widely grown crop, with the location of ethanol plants. The local use of corn oil produced at these ethanol plants for fuel needs in agriculture has great potential to improve both economics and sustainability.

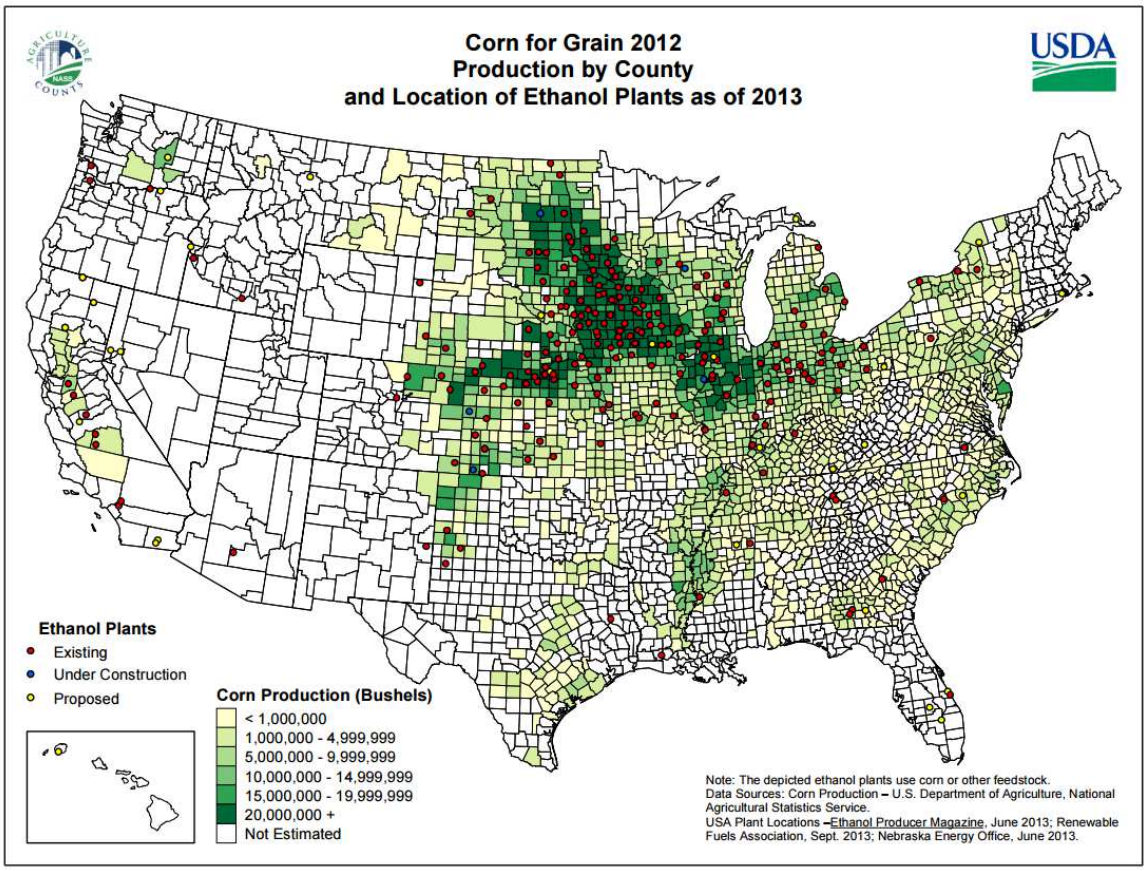

Figure 6-1. U.S. corn production and ethanol plants

6.3 Fuel pathway conclusions

6.3.1 SVO and Dilution Mixtures

SVO and dilution mixtures were not used in engine testing, only as baseline for the fuel property evaluation. Farmers looking to grow one of these oilseeds for on-farm fuel needs should also consider converting the fuel (physically or chemically) before using it in their equipment. Most scientific literature is in agreement that long-term use of SVO or dilution mixtures can be detrimental in a modern diesel engine. The fuel property testing done here found much higher viscosity for the SVOs than petrodiesel. Even after heating the SVO, as is done with many engine conversion kits, the viscosity is still much higher than petrodiesel [81] [91]. For the same blend ratio, TGBs were shown to be better at reducing viscosity and improving cold flow characteristics than the dilution method.

6.3.2 TGBs

The main advantage to TGBs over the fuel pathways using a chemical conversion is that they are much easier to produce. Without a chemical conversion, the process of making fuel can continually flow without the need for batch production. The physical conversion to TGBs is also not as energy intensive, as they can be splash blended at atmospheric pressure and temperature. Equipment costs will be less to set up a TGB production plant than B100 plant (no reactor, no wash tank, no methoxide tank, etc.). The raw materials involved along with the low pressure and temperature also make for a safer conversion. Producing B100 involves using chemicals that can cause burns, blindness, and fire hazards and therefore may see storage or other restrictions in some areas [194] [195]. Gasoline as a blending agent is easier to find in rural areas than the raw products to make B100 (i.e. methanol and potassium hydroxide). TGB production does not produce the co-product glycerol, which may be difficult for farmers to market or dispose of. Finally, a wash step is not needed for TGB production, which in B100 production creates wastewater or filtering media that must be properly disposed of.

Engine performance testing of TGBs was found to be generally acceptable. In many categories such as thermal efficiency, heat release rates, and fuel consumption, a 75/25 TGB performed similarly or slightly better than B100 of the same feedstock. The TGBs had lower NOx emissions than B100, but had higher HC and PM levels at the load and speed tested. Additional testing could further quantify TGB emissions at a wider range of engine operating conditions.

Several important lessons learned were obtained about the blending ratio and blending type for TGBs during fuel property testing. Although blending SVO with higher levels of gasoline-ethanol blends (i.e. E85) was shown to be technically feasible, the possibility of separation

necessitates limiting the level to E10. TGBs formed using E10 were shown to be chemically stable through one year of storage. Another unique trait about TGBs is that by changing the blend ratio, fuel properties can be somewhat tailored depending on time of year, engine application, and economics (cost of gasoline versus the oil).

6.3.3 B100

B100 engine performance was also favorable. Like other researchers have found, B100 has emission benefits in some categories as compared to petrodiesel.

Most engine manufactures now certify their engines for biodiesel blends between 2-20% if the biodiesel used in the fuel blend meets the standards of ASTM D6751. This may be a major advantage for B100 over TGB if a farmer is primarily operating newer equipment still under warranty. Farmers considering industrial oilseed based biofuels of any type must consult their equipment manufacturer's warranty statement.

Additionally, if a producer gets their fuel certified and pays applicable taxes, they may be able to legally use the fuel on-road since B100 is an approved U.S. EPA fuel pathway for many feedstocks [196]. This may be significant for some farmers with large on-road diesel fuel needs. Historically, producers of B100 have been able to apply for a $1/gallon income tax credit, although that incentive is not guaranteed in future years [197]. There may be other incentives at the state or local level for B100 producers.

6.3.4 R100

The U.S. military and transportation sector would like biofuels to be "drop-in" alternatives to petroleum. The R100 engine performance during this study was nearly identical to petrodiesel, but with emissions benefits in some categories. The drop-in characteristics have several benefits. Not only is engine performance very similar to petrodiesel, the fuel can use the same

transportation infrastructure as petrodiesel. The lack of oxygen in the fuel results in excellent oxidative stability and cold weather flow properties.

One downside to the R100 pathway is it may not be a feasible conversion for farm-scale fuel production. The complexity and initial cost of the conversion method may limit its use to larger commercial scale operations.

6.4 Recommendations for future work

6.4.1 Additional engine performance testing

As discussed earlier, the TGBs had slightly elevated HC and PM emissions during engine testing. Future testing at other engine modes (load and speed) will better quantify its performance over a wider range of operating conditions.

The use of renewable naphtha showed great potential in the engine performance studies and fuel property testing of this research. Future work should continue to investigate naphtha in parallel to E10 as blend agents for making TGBs.

6.4.2 Durability studies

Long-term durability testing is necessary to assess the impact of using TGBs in the combustion chamber, fuel system, and after-treatment components. Some durability studies have been already been completed at the EECL, and will be documented in future publications [187]. Future work should concentrate on how the blend ratio of the TGB affects durability. Other factors that should be explored in future research are the effect of filtering, refining, and pretreatments on TGB durability. During the short-term engine performance studies of this research, there were no statistical difference between using crude and refined, bleached, and deodorized (RBD) oils as feedstock. Durability testing would reveal if any differences arise after longer-term use.

Future durability testing should also monitor the effects of new fuel pathways on after-treatment components through equivalent aging studies. Most modern diesel engines use sophisticated exhaust filters and catalysts to meet stringent requirement of later tiers of U.S. EPA emission standards. Many engine manufactures already limit the level of biofuel blends due to the sensitively of this equipment. For example, John Deere restricts biodiesel blends above B20 for their engines with exhaust filters due to risks that "include, but are not limited to, more frequent regeneration, soot accumulation, and increased intervals for ash removal" [198]. Figure 6-2 shows the complexity of a typical Tier 4 after-treatment system. These components must be protected, not only for the important job they perform for emissions control, but also for their large replacement cost. For heavy-duty engines, the estimated cost for emission controls is 1-3% of the total equipment price [199].

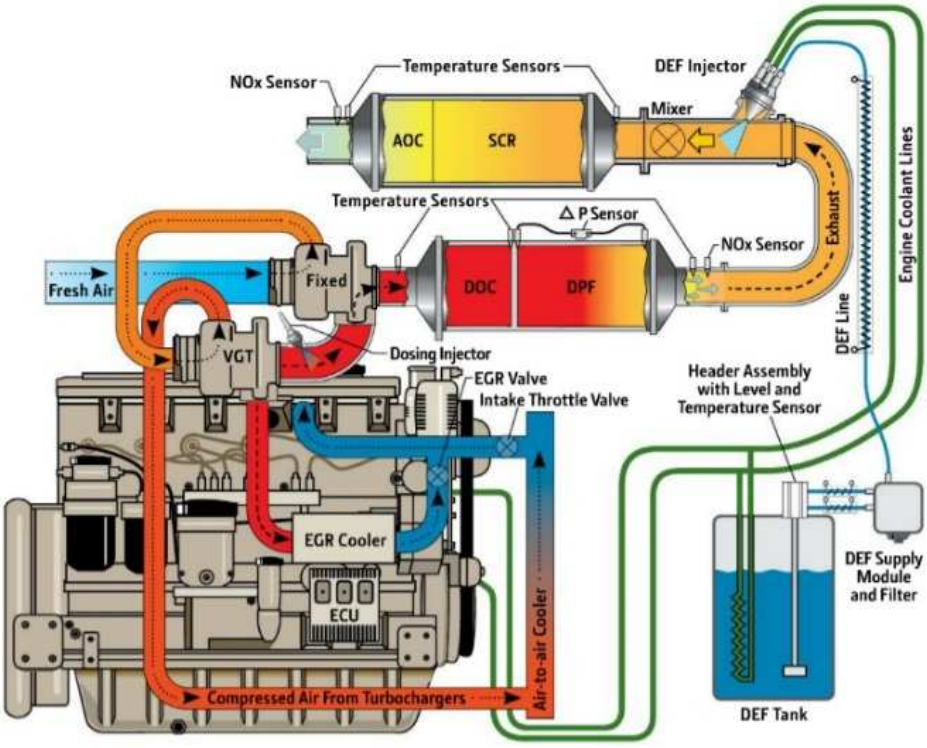

Figure 6-2. John Deere PowerTech 4.5L Tier 4 exhaust aftertreatment system [200]

6.4.3 Fuel property testing

The fuel property testing of this report was fairly extensive. Several key parameters were measured for all fuel types. Since no ASTM standard exists for TGBs, the standards of petrodiesel and biodiesel were used as comparisons. However, some fuel properties in the ASTM standards were not measured due to equipment availability or financial constraints. Future work should include exploring other fuel properties not measured here. The measurement of cetane number for a blend sweep of TGBs would be beneficial to confirm recommendations made based on engine performance testing. The testing of TGBs for metals or other impurities known to poison exhaust system catalysts should also be done in future work. Initial testing of TGB lubricity was favorable; additional blend sweep testing would determine blend ratio's effect on lubricity.

6.4.4 Oil extraction studies

Oil extraction is a vital step between the harvest of an oilseed and the conversion of that oil into a biofuel. Oils must readily extracted from the seeds in an efficient and economic manner. Future oil extraction studies would be beneficial to ensure the industrial oilseeds in this report are compatible with existing crushing and oil extraction methods used at farm-scale so they can be easily adapted. The resulting meal and other coproducts (straw, etc.) should also be analyzed to determine its value as animal feed or in other markets.

6.4.5 Flammability and safety testing

Future testing of the flammability limits of TGBs will be beneficial to better quantify the flammability of TGBs in a fuel tank and storage container. Initial flashpoint testing has shown TGBs should be treated as a Class I (flammable) liquid. Operators looking to use TGB must be

familiar with their fuel system and application to determine if any modifications are warranted such as the fitting of fire arresters on fuel tanks.

6.4.6 Agronomic studies

Plant scientists should continue to improve the genetics of these new industrial oilseeds. The fuel production of these oilseeds should be maximized, which includes overall yield and oil percentage within the seeds. Plant scientists should also be mindful of oil quality so in future years these oilseeds can fully meet all requirements of both ASTM D6751 and EN 14214 without additives. Another area of focus is to help these plants fit into the cropping systems outlined in section 1.4. This would include reducing the growing season and selecting varieties that can best withstand low-input cropping systems.

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